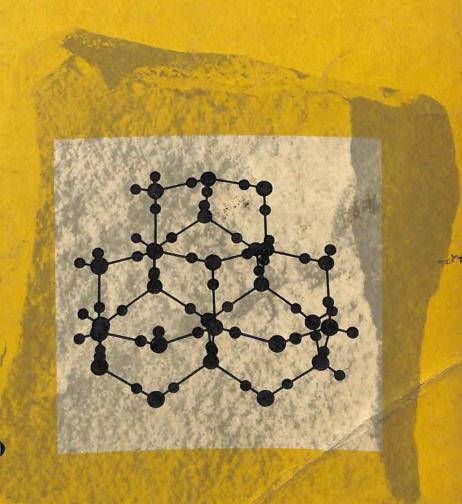
New trends in chemistry teaching

Tendances nouvelles de l'enseignement de la chimie

Volume II

L'enseignement des sciences fondamentales Chimi The teaching of basic sciences



Unesco



The teaching of basic sciences L'enseignement des sciences fondamentales

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New trends in chemistry teaching

Tendances nouvelles de l'enseignement de la chimie

Vol. II



Edited for Unesco/Préparé pour l'Unesco by/par E. Cartmell Deputy Director of Laboratories Department of Chemistry University of Southampton United Kingdom



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SC.68/XIV.II.5/AF Printed in Belgium Promotion of the exchange of information on the content and methodology of science teaching forms an important part of Unesco's programme to develop and improve science education at all levels. To this end Unesco is publishing, within the collection *The Teaching of Basic Sciences*, a series of volumes entitled *New Trends in...*, which consist of papers and articles from leading science-teaching journals on content, curricula, approaches and techniques in the teaching of the three basic sciences—physics, chemistry and biology—and mathematics.

The four volumes published in 1967-68 represented a first experiment to find the best means of placing useful information on basic science teaching in the hands of as many science educators as possible at minimum cost and delay. Although the volumes were intended mainly for teachers in universities and teacher-training institutions, experience has shown that they can also help secondary-school teachers in their difficult task of keeping abreast of the rapid developments taking place in curricula, syllabuses, methods and materials for science teaching, as well as university students of chemistry who are training to be teachers. Science educators in national science teachers' associations, in ministries of education and in examinations boards are also likely to find the information helpful.

This second volume on New Trends in Chemistry Teaching presents papers originally published during 1966 and 1967 in leading chemistry-teaching periodicals of the world. A much wider representation of journals has been achieved than in the first volume. Unesco asks for the continued help of readers in assuring an even more international character for subsequent volumes. It gratefully acknowledges the readiness with which editors and publishers of journals have given permission for the reproduction of papers.

To simplify the use of this volume, the papers have been grouped in sections: structure, energetics and kinetics, acids and bases, organic chemistry, electrochemistry, chemistry and industry, etc. This grouping should facilitate the task of introducing new topics into the chemistry syllabus as well as that of bringing subject matter up to date. Separate introductions have been written for each group of papers to make clear the significance of the papers within the group.

La promotion des échanges de renseignements sur le contenu et la méthodologie de l'enseignement des sciences constitue une partie importante du programme de l'Unesco en faveur du développement et de l'amélioration de l'enseignement des sciences à tous les niveaux. A cette fin, l'Unesco publie dans la collection « L'enseignement des sciences fondamentales » une série de volumes intitulés Tendances nouvelles de..., qui rassemblent des communications et des articles publiés dans les principales revues d'enseignement des sciences et portant sur le contenu, les programmes, les conceptions générales et les techniques de l'enseignement des trois sciences fondamentales — physique, chimie, biologie — et des mathématiques.

Les quatre volumes publiés en 1967-1968 représentent une première expérience ayant pour but de trouver le meilleur moyen de fournir des informations utiles sur l'enseignement des sciences fondamentales au plus grand nombre possible d'éducateurs pour une dépense minime et dans un délai très court. Ces volumes s'adressent principalement aux professeurs des universités et des écoles normales, mais il est apparu que les professeurs de l'enseignement secondaire y trouvent un moyen de se tenir plus facilement au courant des changements rapides intervenant dans les programmes, dans l'organisation des études, dans les méthodes et le matériel d'enseignement des sciences, et qu'ils peuvent également rendre service aux étudiants en chimie qui se destinent au professorat. Les éducateurs appartenant aux associations nationales de professeurs de sciences ou aux services des ministères de l'éducation et ceux qui siègent dans les jurys d'examen y puiseront sans doute aussi des renseignements qui leur seront utiles.

Ce second volume sur les Tendances nouvelles de l'enseignement de la chimie reproduit des communications publiées pour la première fois en 1966 et 1967 dans les principales revues mondiales d'enseignement des sciences. Les périodiques représentés sont beaucoup plus nombreux que dans le premier volume. L'Unesco demande à ses lecteurs de continuer à lui apporter leur concours afin de donner aux volumes qui suivront un caractère encore plus international. Elle exprime sa reconnaissance aux directeurs et éditeurs de revues qui ont bien voulu autoriser la reproduction des textes.

This volume has been prepared in close collaboration with the Committee on the Teaching of Chemistry of the International Union of Pure and Applied Chemistry (IUPAC). Unesco acknowledges with deep gratitude the work of the editor, Mr. E. Cartmell of Southampton University (United Kingdom), who also served as editor of the first experimental volume; he was recommended to Unesco for this work by the Committee on the Teaching of Chemistry of IUPAC.

The choice of papers and articles, their presentation and the opinions expressed in them are the responsibility of the editor and the authors.

The designations employed and the presentation of the material in this list do not imply the expression of any opinion whatsoever on the part of the Unesco Secretariat concerning the legal status of any country or territory, or of its authorities, or concerning the delimitations of the frontiers of any country or territory.

Pour simplifier l'utilisation de ce volume, les articles ont été groupés en sections: structure, énergétique et cinéțique, acides et bases, chimie organique, électrochimie, chimie industrielle, etc. Ce classement facilitera l'inclusion de nouveaux thèmes dans les programmes de chimie ainsi que la mise à jour de certains sujets. Chaque groupe d'articles est précédé d'une introduction destinée à préciser la signification des textes qu'il contient.

Cet ouvrage a été réalisé en collaboration étroite avec le Comité de l'enseignement de la chimie de l'Union internationale de chimie pure et appliquée (UICPA). L'Unesco exprime sa profonde gratitude à M. E. Cartmell, de l'Université de Southampton (Royaume-Uni), qui en a dirigé la publication comme il l'avait fait pour le premier volume expérimental; cette tâche lui avait été confiée sur la recommandation du Comité de l'enseignement de la chimie de l'UICPA.

Le choix des communications et des articles, leur présentation et les opinions exprimées engagent la seule responsabilité du directeur de la publication et des auteurs.

Les désignations employées et la présentation adoptée ici ne sauraient être interprétées comme exprimant une prise de position du Secrétariat de l'Unesco sur le statut légal ou le régime d'un pays ou d'un territoire quelconque, non plus que sur le tracé de ses frontières.

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CANADA

Canadian Chemical Education, The Chemical Institute of

Canada.

FRANCE

Bulletin de l'Union des physiciens.

FEDERAL REPUBLIC OF GERMANY/ RÉPUBLIQUE FÉDÉRALE D'ALLEMAGNE

Der Mathematische und Naturwissenschaftliche Unterricht (MNU), Ferd. Dümmlers Verlag, Bonn.

EASTERN GERMANY/ ALLEMAGNE ORIENTALE

Chemie in der Schule, Volk und Wissen Volkseigener Verlag, Berlin.

HUNGARY/HONGRIE

A Kémia Tanitása.

JAPAN/JAPON

Chemical Education, Chemical Society of Japan.

Nigeria/Nigéria

Journal of the Science Teachers Association of Nigeria, The Science Teachers Association.

SWEDEN/SUÈDE

Elementa, Stiftelsen Elementa.

SWITZERLAND/SUISSE

Mitteilungen der Vereinigung Schweizerischer Naturwissenschaftslehrer.

U.S.S.R./URSS

Himija v Škole, Ministerstvo Prosveščenija, R.S.F.S.R.

UNITED KINGDOM/ROYAUME-UNI

Chemistry in Britain, Royal Institute of Chemistry. Education in Chemistry, Royal Institute of Chemistry. The School Science Review, Association for Science Education.

UNITED STATES OF AMERICA/ ÉTATS-UNIS D'AMÉRIQUE

Chemistry, The American Chemical Society. Journal of Chemical Education, The American Chemical Society.

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1. Bonds and structures

1. Liaisons et structures

The purpose of these editorial introductions to the main sections of this volume is to indicate the reasons underlying the selection of particular topics, and the relevance of the topics to chemistry teaching at different levels. The opportunity will also be taken to refer to other useful papers which have not been included in the main text.

The content lists of recent textbooks of general chemistry reveal that most writers agree on the topics that must be dealt with as a preliminary to a discussion on structure and bonding. These include interaction of light with matter, ionization potentials and electron affinities, the charge-cloud model, polar and non-polar molecules, electrovalency and covalency, electronegativity, the ionic character of bonds, etc. Volume 1 of New Trends in Chemistry Teaching contained a number of articles on valency theory, atomic and molecular structure and related topics. Some of these were at a relatively advanced level and were intended for first-year college students, teachers in training or as refresher courses for older teachers. It is hoped that the articles in the present volume, which have in many cases been selected to present these topics at a more elementary level, will be read in conjunction with those in the earlier volume.

VALENCY

Students of all ages often find difficulty in grasping the concepts of valency and oxidation number. To some extent the difficulty arises from an attempt "to establish a single allembracing definition of the valency of an atom in a molecule or ion". H. C. Longuet-Higgins, in the article reproduced here, points out that valency can be used to signify two distinct concepts: "electrovalency" and "covalency". If simple definitions are adopted to obtain numbers for these two types of valency many of these apparent anomalies disappear.

Les introductions aux principales sections de ce volume ont pour objet d'indiquer les raisons qui ont présidé au choix de certains thèmes et de montrer leur intérêt pour l'enseignement de la chimie aux différents niveaux. Elles fourniront également l'occasion d'évoquer d'autres textes utiles qui n'ont pas été inclus dans le recueil.

En comparant les tables des matières de récents manuels de chimie générale on constate que la plupart des auteurs s'accordent sur les thèmes qui doivent être traités préalablement à l'étude de la structure et des liaisons. Ce sont l'interaction de la lumière et de la matière, les potentiels d'ionisation et les affinités électroniques, le modèle de nuage électronique, les molécules polaires et non polaires, l'électrovalence et la covalence, l'électronégativité, les liaisons partiellement électrovalentes, etc. Le volume 1 des Tendances nouvelles de l'enseignement de la chimie contenait un certain nombre d'articles sur la théorie de la valence, sur la structure atomique et moléculaire et sur des sujets connexes. Une partie de ces textes, d'un niveau relativement élevé, s'adressaient aux étudiants de première année de l'enseignement supérieur, aux élèves des écoles normales ou aux professeurs d'un certain âge suivant des cours de recyclage. Ceux du présent volume ont été choisis, le plus souvent, de manière à donner un exposé plus élémentaire de ces mêmes thèmes et il est recommandé de les lire en se référant aux articles du volume précédent.

VALENCE

Les étudiants de tous âges éprouvent souvent des difficultés à assimiler les notions de valence et de degré d'oxydation. Dans une certaine mesure, l'obstacle vient de ce qu'on s'efforce d'«établir une définition unique et universelle de la valence d'un atome dans une molécule ou un ion ». H. C. Longuet-Higgins, dans l'article qu'on trouvera reproduit ici, souligne que le terme de valence peut être utilisé dans deux acceptions distinctes — « électrovalence » et « covalence ». Si l'on adopte des définitions simples afin d'obtenir des degrés d'oxydation correspondant à ces deux types de valence, beaucoup d'anomalies apparentes disparaissent.

IONIZATION POTENTIALS

There are two particularly important sources of experimental data that support the quantum theory of atomic and molecular structure. These are experimental spectroscopy, in which the absorption of radiation is used as a method of measuring differences in energy levels, and measurements of ionization potentials. Attempts to introduce concepts such as elementary quantum theory and the charge-cloud model into school teaching are often criticized because these ideas cannot easily be shown to follow from experiment. However, the hydrogen atom line spectrum can be demonstrated with the help of an inexpensive replica diffraction grating, and this experiment can be used with senior classes to support the theory of discrete energy levels in atoms.

Measurements of ionization potentials, which reveal very clearly, with quite simple equipment, the energy needed to remove particular electrons from atoms are especially helpful in providing a basis for discussing electron configurations and the numbers of electrons in completely filled shells. Experiments of this kind indicate, for example, the reason for the "inert" character of the noble gases, and that one electron can be removed from an alkali metal atom more readily than any subsequent ones. (In passing, it might be noted that, contrary to the impression given in many textbooks, quite a large amount of energy is needed to remove one electron from such an atom.) An article by R. S. Nyholm and B. E. Dineen (Proc. Roy. Inst. Chem., 1963, p. 110) gives full details of some experiments on measuring ionization potentials suitable for use in schools. The article by G. Couchet and A. Zvenigorosky reproduced here is somewhat more sophisticated, but it explains very clearly some of the different techniques that have been developed from the classical experiments of Franck and Hertz to get precise measurements of successive ionization potentials.

POLAR AND NON-POLAR SUBSTANCES

The article by T. Theimann describes a simple experiment that is becoming well known in school chemistry courses. This experiment shows in a simple and direct way that the electrical properties of water differ markedly from those of carbon tetrachloride, benzene and many other organic liquids. It is tempting to ascribe the different deflections of liquid streams in the same external electric field to the "polar" nature of water and the non-polar nature of carbon tetrachloride. This is probably legitimate at an elementary level, although it must be remembered that non-polar liquids might also be deflected by the field if their molecules happened to have a high polarizability.

ELECTRONEGATIVITY

This topic is mentioned here although there is no article on electronegativity in the main section. Electronegativity is an extremely important topic in all branches of chemistry, but attempts to use it in a quantitative form can be dangerously

POTENTIELS D'IONISATION

Il existe deux sources particulièrement importantes de données expérimentales venant à l'appui de la théorie quantique de la structure atomique et moléculaire. Ce sont, d'une part, la spectroscopie expérimentale, qui utilise l'absorption de radiation pour mesurer les différences de niveaux d'énergie, et, d'autre part, la mesure des potentiels d'ionisation. Les tentatives faites pour introduire dans l'enseignement scolaire des notions comme celles de la théorie quantique élémentaire et du modèle de nuage électronique sont souvent critiquées, car il est malaisé de démontrer l'origine expérimentale de ces idées. On peut néanmoins faire observer les raies du spectre de l'atome d'hydrogène au moyen d'un réseau de diffraction double, instrument peu coûteux, et cette expérience pourra servir dans les classes supérieures à justifier la théorie des niveaux d'énergie discrets dans les atomes.

La mesure des potentiels d'ionisation, qui met en évidence, avec un matériel très simple, l'énergie nécessaire pour arracher des électrons à un atome, est une méthode particulièrement utile fournissant des bases pour l'étude des configurations électroniques et du nombre des électrons dans les couches complètement remplies. Les expériences qui en relèvent expliquent, par exemple, le caractère « inerte » des gaz nobles, et montrent qu'un électron donné d'un atome de métal alcalin peut en être arraché plus facilement que n'importe quel électron suivant. (A noter en passant que, contrairement à l'impression donnée par de nombreux manuels, il faut une très forte quantité d'énergie pour arracher cet électron.) Un article de R. S. Nyholm et B. E. Dineen (Proc. Royal Inst. Chem., 1963, 110) expose en détail certaines expériences sur la mesure des potentiels d'ionisation qui peuvent être pratiquées dans les écoles. L'article de MM. Couchet et Zvenigorosky reproduit ici est un peu plus complexe, mais il explique très clairement certaines des techniques qui ont été mises au point à partir des expériences classiques de Franck et Hertz pour obtenir des mesures précises des potentiels d'ionisation successifs.

SUBSTANCES POLAIRES ET NON POLAIRES

L'article de Th. Theimann décrit une expérience facile qu'on commence à bien connaître dans les classes de chimie. Elle démontre d'une manière simple et directe que les propriétés électriques de l'eau diffèrent considérablement de celles du tétrachlorométane, du benzène et de nombreux autres liquides organiques. Il est tentant d'attribuer les déviations différentes de filets liquides placés dans le même champ électrique extérieur à la nature « polaire » de l'eau et à la nature non polaire du tétrachlorométane. Cette explication est probablement légitime au niveau élémentaire, mais il faut se souvenir que les liquides non polaires peuvent aussi être déviés par le champ si leurs molécules se trouvent être fortement polarisables.

ÉLECTRONÉGATIVITÉ

Nous mentionnerons ici ce thème bien que le recueil ne comprenne pas d'article sur l'électronégativité. Cette notion est extrêmement importante pour toutes les branches de la chimie, mais on risque de commettre de dangereuses erreurs à vouloir misleading. Reference may be made to two recent articles which discuss electronegativity in the context of school chemistry: "The Concept of Electronegativity", School Science Review, No. 161, 1965, p. 71; and: "An Experiment on the Teaching of Electronegativity", A Kemia Tanitasa, Vol. 5, No. 2, 1966, p. 57 (an English translation from this Hungarian journal is available from the Division of Science Teaching of Unesco).

A recent paper by R. G. Pearson (Chemical Communications, 1968, p. 65) highlights the dangers of using Pauling's thermochemical approach in using electronegativity values to calculate heats of formation, etc. Thus in the reaction

$$LiF(g) + CsI(g) \rightarrow LiI(g) + CsF(g)$$

electronegativity values predict $\Delta H = -21~\rm kcal/mole$, thus expressing the tendency for the least electronegative element Cs to combine with the most electronegative element F. Unfortunately the experimentally determined ΔH value for this reaction is $+17~\rm kcal/mole$, and the important factor is probably the strong electrostatic attraction between two small atoms, Li and F. Thus, while a general appreciation of electronegativity trends across a period or down a group in the periodic table is very desirable, teachers should avoid attempts to extend the range of this concept in such things as estimations of ΔH , calculations of the ionic character of bonds, and so on.

HYDROGEN BONDS

Structures in which units (single molecules, polymer chains, networks) are held together in a regular pattern by hydrogen bonds are of great practical importance (particularly in biochemical systems). The article on hydrogen bonding included in this section is unusual in that it presents a literary and philosophical approach to the topic of a type that does not often appear in the scientific literature, unfortunately. This approach should be especially useful for teachers who are introducing aspects of science into "liberal arts" courses.

MODELS

The teaching of structural chemistry only comes to life if it is accompanied by model construction by the pupils themselves. Volume 1 of New Trends included an article on building models from polystyrene foam spheres. The two articles included in the present section have been selected because they are particularly relevant to situations where there is very little money for equipment. "Milk straws" are readily available all over the world, and the framework models from them, if fragile, are particularly elegant.

l'employer sous forme quantitative. Nous renvoyons le lecteur à deux articles récents qui étudient l'électronégativité dans le contexte de l'enseignement scolaire de la chimie: « The concept of electronegativity », School science review, n° 161, 1965, p. 71, et « An experiment on the teaching of electronegativity », A Kemia Tanitasa, vol. 5, n° 2, 1966, p. 57 (on peut se procurer la traduction anglaise de ce périodique hongrois à la Division de l'enseignement des sciences de l'Unesco).

Un article récent de R. G. Pearson (Chemical communications, 1968, p. 65) met en lumière les dangers de l'emploi de la méthode thermochimique de Pauling, qui utilise les électronégativités pour calculer les chaleurs de formation, etc. Ainsi dans la réaction

$$LiF(g) + CsI(g) \rightarrow LiI(g) + CsF(g)$$

les électronégativités laissent prévoir $\Delta\,H\!=\!-21$ kcal/mole, exprimant ainsi la tendance de l'élément le moins électronégatif > (Cs) à se combiner avec l'élément le plus électronégatif (F). Malheureusement, la valeur de $\Delta\,H$ déterminée expérimentalement pour cette réaction est +17 kcal/mole, ce qui doit tenir surtout à la forte attraction électrostatique s'exerçant entre deux petits atomes comme Li et F. S'il est très souhaitable d'avoir une connaissance générale de l'échelle d'électronégativité correspondant à une période ou à un groupe du tableau périodique, les professeurs auraient néanmoins intérêt à éviter d'étendre l'emploi de cette notion à certaines opérations telles que l'estimation de $\Delta\,H$, le calcul de l'électrovalence partielle des liaisons, etc.

LIAISONS HYDROGÈNE

Les structures où la cohésion des unités élémentaires (molécules uniques, chaînes polymériques, réseaux) et la régularité de leur arrangement sont assurées par des liaisons hydrogène présentent une grande importance pratique (en particulier dans les systèmes biochimiques). L'article sur la liaison hydrogène reproduit dans cette section offre l'originalité d'exposer le sujet sous un angle littéraire et philosophique, ce qui est malheureusement rare dans la littérature scientifique. Cette approche devrait être particulièrement utile aux professeurs qui, dans un enseignement essentiellement classique, font une place aux aperçus scientifiques.

MODÈLES

L'enseignement de la chimie structurale ne devient vivant que s'il s'accompagne de la construction de modèles par les élèves eux-mêmes. On trouvera, dans le volume 1 des Tendances nouvelles, un article sur la réalisation de modèles au moyen de sphères en mousse de polystyrène. Les deux articles reproduits dans la présente section ont été choisis en raison de l'intérêt particulier qu'ils présentent pour les établissements n'ayant que très peu d'argent à consacrer à l'achat de matériel. Les « pailles » artificielles se trouvent facilement dans le monde entier et permettent de construire des modèles à baguettes qui sont sans doute fragiles mais très esthétiques.

WHEN IS AN ATOM ZERO-VALENT?

By H. C. Longuet-Higgins, M.A., D.PHIL., F.R.I.C., F.R.S.

Professor of Theoretical Chemistry, University Chemical Laboratory, Cambridge

In the good old days when the chemical bond was just a line between two atoms, there was no difficulty in defining the valency of an atom in a molecule:

molecule	9	H-O-H		Na	-Cl
atom		но		Na	Cl
valency		1 2		1	1
	H_4N	T-Cl	N =	N = 0)
		l Cl	N	N C)
	5	1	3	5 2	

With a few exceptions:

each element seemed to possess a small number of possible valencies (e.g. 3 and 5 for nitrogen) which determined the structures of its simpler compounds.

With developments in ionic theory chemists began to wonder whether they ought not to replace some of the lines in their structural formulae by pairs of electric charges:

$$Na^{+}Cl^{-}H_{4}N^{+}Cl^{-}R_{3}P^{+}O^{-}$$

This notation was put on a firm basis by the electronic theory of valency, in particular by the octet rule for first-row atoms, but it reopened the question of how one should define the valency of an atom in a given molecule or ion. One could, of course, define the valency as the number of electron-pair bonds, n, plus the magnitude |q| of the formal charge, q, associated with the atom:

but this definition had its drawbacks. For instance, the removal of a proton from NH_3

would not change the valency of the N atom, but addition of a proton would increase it by 2:

More seriously, however, the definition implied that the valency of a metal ion could be substantially increased by simple co-ordination:

$$n \,+\, |q|$$
 for Hg atom $\begin{array}{ccc} \mathrm{Hg^{2+}} & \mathrm{I} \\ \mathrm{I} & \mathrm{I} \end{array}$

In his classic book The Electronic Theory of Valency, Sidgwick recognized the difficulties of defining the valency of an atom in a molecule within the context of the classical electronic theory, but suggested that the best compromise would be to define the valency of an atom in a given species as the number of unshared electrons in the valency shell of the free atom minus the number of unshared electrons in the valency shell of the combined atom. This amounts to defining the valency as (n+q) rather than (n+|q|), where n is the number of electron-pair bonds to the atom and q is the formal positive charge. With this definition the valency of a metal ion is unchanged by simple co-ordination:

$$(n+7q)$$
 for Hg atom $(n+7q)$ $(n+7q)$

but the valencies of electronegative atoms vary capriciously between closely related compounds:

and even between alternative plausible structures for the same compound:

Sidgwick himself pointed out that this definition of valency makes the oxygen atom in the methoxide ion zero-valent; but he felt this to be an allowable fault in a definition which 'correctly' assigns a valency of 2 to the iron atom in the ferrocyanide ion:

$$\begin{array}{cccc} \text{ion} & \dots & \text{Fe$^{2+}$} & \text{Fe$^{4-}(-C \equiv N)_6$} \\ (n+q) \text{ for Fe} & 2 & 2 & 2 \end{array}$$

One might, nevertheless, feel dissatisfied with a state of affairs in which the nickel atom in nickel carbonyl could be assigned a valency of 0 or 8 according as one regards it as coordinated or doubly-bonded by the ligands; and in the following paragraphs I shall suggest a point of view which goes some way towards eliminating such difficulties.

According to this point of view one should not try to establish a single all-embracing definition of the valency of an atom in a molecule or ion, but should recognize that the word 'valency' can be used to signify either of two distinct, but equally useful, concepts. The first is Sidgwick's (n+q), which we may call the 'electrovalency'; the second is the quantity (n-q), which is appropriately described as the 'covalency'. We have already seen that the electrovalency is a useful concept for a co-ordinated metal ion; but in order to bring out the distinction between the two concepts and the significance of each, let us tabulate the electrovalencies and the covalencies of various atoms in some of the molecular species already mentioned. It will be remembered that q is the formal positive charge and n is the number of electron-pair bonds to the atom:

For the electronegative N and O atoms in these species the covalency is seen to be a satisfactory concept. Now for some molecules with alternative resonance structures:

In these species also the covalency has the invariant value 3 for N and 2 for O, but for P in a phosphine oxide and for C in carbon monoxide the covalency is variable and it is the electrovalency which is the same for the two resonance structures, namely 5 for P and 2 for C. In this sense it is appropriate to say that the P atom in R₃PO is in a higher state of oxidation than the P atom in R₃P, and that the C atom in CO is in a lower state of oxidation than the C atom in CO₂ where the electrovalency is 4; but one must be careful with such statements, since the C atom in CH₄ also has an electrovalency of 4.

Turning to more complex cases:

we again discover that when there is resonance between different structures an atom involved in the resonance usually differs either in electrovalency or in covalency, but not in both, between the various structures. More specifically, acceptance of a co-ordinate link from a ligand increases the covalency of an atom but leaves its electrovalency unchanged (this was the rationale of Sidgwick's definition) whereas donation of a co-ordinate link, e.g. by back-coordination from the Ni

in Ni(CO)₄, raises the electrovalency but leaves the covalency unchanged. For a given atom in a given resonance situation either the electrovalency or the covalency is invariant (except in very special cases), and it is the invariant valency with which one will be primarily concerned.

Immediately, however, the question arises: are there any rules for deciding which of the two concepts—electrovalency or covalency—is the one to use in a given structural situation? The short answer is simple: for electropositive atoms one will usually be concerned with the electrovalency, for electronegative atoms with the covalency. But where does one draw the line between electropositive and electronegative atoms? To see that this question is not as simple as it looks, let us consider three compounds of chlorine, which is usually regarded as an electronegative element:

In NaCl and $\mathrm{CH_3Cl}$ the Cl atom has a covalency of 1, the usual covalency of a halogen atom. But in the perchlorate ion the covalency depends on the amount of doublebonding supposed to occur; here the invariant valency is the electrovalency, equal to 7, and it is in this sense that the Cl atom is heptavalent in the ${\rm ClO_4^-}$ ion. The invariance of the electrovalency is an indication that the Cl atom in a perchlorate should be regarded as an electropositive atom rather than an electronegative one, in agreement with the intuition of the inorganic chemist. This example illustrates the general point that in writing resonance structures we are expressing views about the relative electronegativities of the atoms in a molecular species, and the resonance structures indicate whether we should employ the electrovalency or the covalency in discussing the state of any atom in the molecule.

To take another example: in Ni(CO)₄ one usually disregards resonance structures in which the nickel atom is not covalently bound to all four CO groups, but allows contributions from all those structures in which each CO is bound to the Ni atom by a single or a double bond. In these structures, as already shown, the Ni atom has a constant covalency of 8. whereas its electrovalency varies from 8 right down to 0. The invariance of the covalency in the important resonance structures implies that in Ni(CO)4 the Ni atom should be regarded as an electronegative rather than an electropositive atom; in other words, as a multi(co)valent atom rather than a metal atom of low (electro)valency.

It is interesting to try to extend this discussion of nickel carbonyl to other organometallic compounds, especially those of the transition elements. As a guide to the properties of these substances the '18electron rule' has proved most useful, though it has numerous exceptions. According to this rule an organometallic transition-metal compound is likely to be specially stable if the valency shell of each metal atom in the molecule contains as many electrons as the next inert-gas atom. The number of electrons in the valency shell is the sum of three quantities: the number of valency electrons in the free atom, the formal negative charge on the combined atom and the number of electron-pair bonds to the neighbours. The sum of the last two of these quantities is just the covalency as we have defined it, so the 18-electron rule will be satisfied if the covalency is invariant and equal to 18-z, where z is the number of valency electrons of the free metal atom. For the atoms of the first transition series the most stable covalencies are accordingly:

but there are, of course, many organometallic compounds of these elements where the covalency is greater or less than 18-z.

Viewed in this way, the 18-electron rule is seen to have exactly the same standing as the octet rule for the first-row atoms of the Periodic Table. The octet rule asserts that compounds of C, N, O and F are particularly

stable if each of these atoms has a covalency equal to 8-z, where z is the number of electrons in the valency shell of the free atom. One might even suggest that the special position of C, for which 8-z=z, is imitated by Co, for which 18-z=z; the organometallic compounds of cobalt conform to the 18-electron rule with exceptional fidelity.

We are now in a position to consider the question: when is an atom zero-valent? The best answer seems to be that a free atom is trivially zero-valent, but that when an atom enters into chemical combination one must distinguish between its electrovalency and its covalency, and must bear in mind that these concepts are only defined relative to a particular resonance structure or set of resonance structures. Subject to these qualifications there are, indeed, a few compounds in which the electrovalency is zero: the Ca atom in Ca(NH₃)₆ is a case in point. But it is

imprecise to describe a transition-metal atom in an organometallic compound as 'zero-valent'; in only a minority of important structures does the metal atom have a zero electrovalency, and the invariant valency is the covalency, which will be relatively large. And in so far as the electrovalency determines the 'state of oxidation' of the atom, the state of oxidation is also uncertain when the atom has a different electrovalency in different structures.

In conclusion it must be pointed out that the concepts of electrovalency and covalency sometimes fail completely, as in decaborane or the allyl radical. This is neither surprising nor regrettable, for new theoretical advances often stem from the failure of earlier concepts. None the less, it is a good thing to define all one's working concepts as clearly as possible, if only to avoid misunderstanding and confusion; that is the relatively humble intention of this paper.

Détermination des Potentiels d'Ionisation par les Méthodes Electriques

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Introduction

Lorsque les atomes ou les molécules d'un gaz raréfié sont bombardés par un faisceau d'électrons, l'ionisation du gaz peut se produire si l'énergie des électrons incidents est supérieure à un certain seuil d'énergie $W_1 = eV_1$, V_1 étant le potentiel d'ionisation du gaz considéré. Cette ionisation s'accompagne d'une émission lumineuse et lorsqu'on analyse cette lumière au spectroscope, on trouve un spectre constitué d'un grand nombre de raies. L'expérience et la théorie montrent que la fréquence la plus élevée v_1 est telle que $W_1 = hv_1$.

La détermination expérimentale des potentiels d'ionisation peut donc s'effectuer au moyen de deux méthodes différentes : la méthode spectroscopique qui consiste à déterminer la longueur d'onde λ_1 correspondant à ν_1 et la méthode électrique. Dans cette dernière, l'apport d'énergie qui provoque le passage d'un atome d'un niveau d'énergie à un niveau plus élevé provient d'électrons qui ont subi une chute de potentiel exactement mesurée. Il suffit alors de déterminer directement la plus petite valeur du potentiel accélérateur pour laquelle on obtient la formation d'ions. Cette méthode électrique peut être mise en œuvre dans la source d'ions d'un spectrographe de masse, ce qui permet de faire à la fois la détermination des potentiels d'ionisation et l'identification des ions au fur et à mesure de leur formation.

(I) - LA METHODE DE FRANCK ET HERTZ

§ 1. Principe de la méthode.

C'est en 1913 que Frank et Hertz ont montré les premiers que lorsque les électrons ont une énergie supérieure à un certain seuil, les molécules du gaz bombardé peuvent être ionisées. La méthode employée utilise le dispositif expérimental schématisé dans la figure 1.

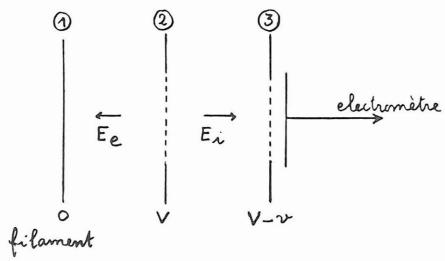


Fig. 1

Les électrons émis par un filament chaud (1) sont accélérés par l'électrode (2) portée au potentiel V. Ils pénètrent alors dans l'enceinte gazeuse où règne une pression de 10⁻² Torr environ. Les ions positifs formés entre les électrodes (2) et (3) sont accélérés par un champ électrique convenable E₁ et sont recueillis par la plaque collectrice d'un électromètre. Le potentiel d'ionisation est la plus petite valeur de V pour laquelle l'électromètre détecte un courant.

Les résultats obtenus par cette méthode sont loin d'être satisfaisants. La courbe donnant l'intensité du courant ionique détecté en fonction de l'énergie des électrons à l'allure indiquée dans la fig. 2.

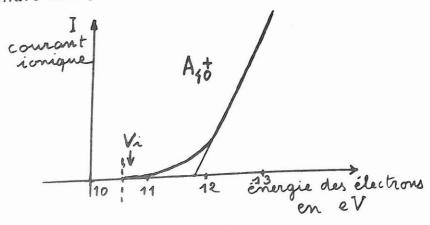


Fig. 2

La courbe présente une partie arrondie, une « queue », s'étendant sur un intervalle de 1,5 volts environ puis une partie rectiligne. La valeur V₁ correspondant à I = 0 ne peut être lue avec précision. De plus cette valeur est très différente de la valeur obtenue par la méthode spectroscopique. Sur la courbe de la figure 2 extraite du mémoire de FOX (1) la valeur du potentiel d'ionisation est différente de plus de 4 volts de la valeur spectroscopique 15,77 volts.

§ 2. Amélioration de la méthode de Franck et Hertz par l'emploi d'un gaz calibrateur.

La critique de cette méthode classique montre que l'allure de la courbe expérimentale et l'erreur commise sur la détermination du potentiel d'ionisation proviennent de l'imprécision avec laquelle l'énergie réelle du faisceau électronique ionisant est connue. En effet lorsque le potentiel de l'électrode (2) est V, l'énergie de tous les électrons ionisants n'est pas eV.

L'étalement en énergie résulte de la distribution en énergie des électrons lors de l'émission à partir du filament chaud, de l'existence de potentiels de contacts entre les électrodes et de l'action du champ accélérateur E₁ qui agit sur les électrons pénétrant dans la région d'ionisation (espace compris entre les électrodes (2) et (3).

Pour essayer d'éliminer ces causes d'erreurs, on peut utiliser un gaz calibrateur dont le potentiel d'ionisation est bien connu par la méthode spectroscopique. On détermine dans le même appareil (avec des conditions expérimentales aussi voisines que possible) le potentiel d'ionisation du gaz à étudier et le potentiel d'ionisation du gaz calibrateur qui est généralement l'argon. La différence trouvée entre le potentiel d'ionisation de l'argon déterminé par la méthode électrique et la valeur spectroscopique constitue un terme correctif que l'on considère comme valable pour le gaz étudié.

La méthode précédente présente encore des inconvénients. Lorsque la calibration est faite séparément, il faut s'assurer que les conditions expérimentales restent inaltérées quand on change le gaz. Cette condition est assez difficile à réaliser dans la pratique, notamment dans le cas où les molécules du gaz étudié peuvent se scinder en fragments et former des couches minces sur les électrodes, modifiant ainsi le potentiel de contact (2). Lorsque le gaz étalon et l'échantillon sont introduits simultanément,

la calibration est plus précise. Mais ce gaz étalon est alors une source constante de bruit de fond et il peut être difficile de connaître les pressions partielles des deux gaz, quantités dont la connaissance est cependant nécessaire à l'établissement des courbes du courant ionique en fonction de l'énergie des électrons (3).

La méthode classique de Franck et Hertz, bien qu'améliorée par l'emploi d'un gaz calibrateur, a été ultérieurement modifiée dans le but de réduire l'étalement en énergie des électrons ionisants. Cet étalement en énergie est dû à diverses causes que nous allons énumérer rapidement en exposant le principe de la méthode du potentiel retardateur.

(II) - LA METHODE DU POTENTIEL RETARDATEUR

§ 1. Les causes de l'étalement en énergie des électrons ionisants.

La dispersion en énergie des électrons ionisants est due à trois causes distinctes :

a) Influence du champ extracteur d'ions E.

Lorsque les champs E. et E. sont établis en permanence il est évident que les électrons après avoir franchi la grille (2) pour pénétrer dans la chambre d'ionisation sont soumis à l'action du champ extracteur d'ions E. Cette action modifie donc l'énergie que ces électrons possédaient au moment de la traversée de la grille (2). Pour supprimer cet effet perturbateur du champ d'extraction E. sur les électrons ionisants, plusieurs auteurs ont proposé d'utiliser des champs E. et E. pulsés et convenablement décalés dans le temps l'un par rapport à l'autre. Lorsqu'on utilise de tels champs, le faisceau d'électrons ionisants est accéléré et ne produit les ions que pendant l'intervalle de temps où le champ E. est coupé. Quand on recueille les ions par établissement de E., c'est au contraire le champ E. qui est supprimé.

b) Influence de la chute de polentiel le long de la cathode.

Si la cathode est à chauffage direct, la chute de potentiel le long de la cathode est une cause d'erreur car le potentiel de l'électrode (1) n'est plus constant en tous ses points. On utilise alors un courant de chauffage pulsé, les mesures étant faites entre deux pulses, quand le courant est nul (4). c) Influence de la dispersion en énergie due à l'émission électronique.

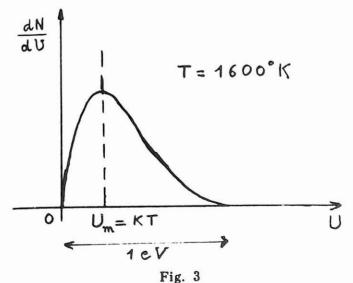
Les deux causes d'erreur précédentes étant éliminées, la dispersion en énergie des électrons ionisants résulte en définitive de la dispersion en énergie liée à l'émission électronique du filament.

On sait que cette distribution, pour des électrons émis par un filament chaud et en prenant un coefficient de transmission égal à l'unité, est donnée par la formule suivante (5) (6):

$$\frac{dN}{dU} = \frac{4 \pi m U}{h^{a}} e^{-\left(\frac{\Phi + \mu + U}{k T}\right)}$$

Dans cette formule U représente l'énergie cinétique des électrons émis, dN le nombre d'électrons émis par cm² et par seconde dont l'énergie est comprise entre U et U + dU quelle que soit la direction de leur vitesse V = U + dU quelle que soit la direction de leur vites V = U + dU quelle que vites V = U + dU quelle que soit la direction de leur vites V

La courbe représentative de cette fonction est indiquée par la fig. 3 pour un filament de tungstène à 1 600°K (3). Il est facile de voir que l'abscisse du maximum de cette courbe correspond à une énergie $U_m = kT$ et que l'étalement en énergie est de l'ordre de l'électronvolt.



Pour réduire cet étalement en énergie, Fox et ses collaborateurs ont proposé une méthode dite méthode du

potentiel retardateur ou méthode R. P. D. (R. P. D. = retarding potentiel différence), (1) (7), que nous allons maintenant exposer.

§ 2. Principe de la méthode R. P. D.

Cette méthode se différencie de la méthode classique par l'addition d'une électrode supplémentaire (1') entre le filament et l'électrode accélératrice des électrons (figure 4).

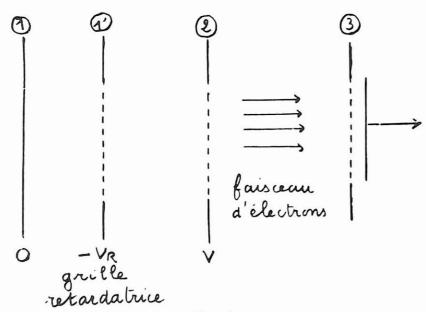
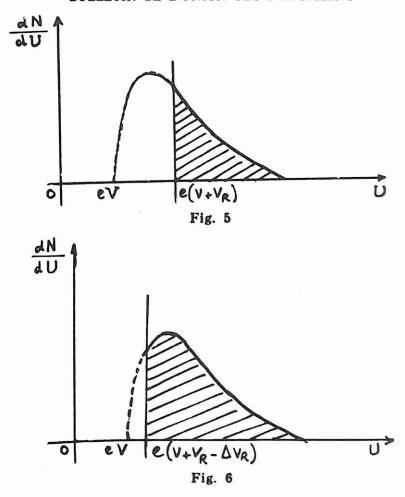


Fig. 4

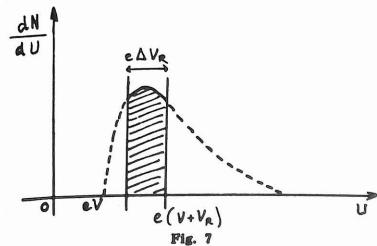
Cette électrode retardatrice est portée à un potentiel Vr légèrement négatif par rapport à celui du filament. Seuls les électrons ayant une énergie cinétique initiale supérieure à eVr franchissent la grille (l'). Si on admet une distribution en énergie initiale identique à celle représentée figure 3 et si l'on admet que l'action du potentiel accélérateur V ne modifie pas la forme de la courbe, la distribution en énergie des électrons à leur entrée dans la région d'ionisation est alors représentée par la figure 5.

La grille retardatrice a pour effet de limiter de manière précise l'énergie inférieure des électrons pénétrant dans la région d'ionisation.

Si maintenant on fait varier le potentiel de la grille (1') d'une petite quantité $+\Delta$ Vr (0,1 Volt en général), la limite du côté des basses énergies sera modifiée et la nouvelle distribution en énergie des électrons pénétrant dans la région d'ionisation sera représentée figure 6.



La différence du nombre d'électrons Δ Ne pénétrant dans la région d'ionisation quand le potentiel de la grille (l') passe de — Vr à — Vr + Δ Vr est représentée par la bande hachurée de la figure 7.



Dans cette bande on dit qu'on a des électrons quasi monoénergétiques. Faisons maintenant varier V en gardant constantes les valeurs de Vr et Δ Vr. Les courbes représentées figures 5, 6 et 7 subissent simplement une translation. La différence du nombre d'électrons pénétrant dans la région d'ionisation reste constante quand Vr varie de Δ Vr. On peut d'ailleurs s'en assurer en mesurant la différence Δ Ie des courants électroniques, Δ Ie restant constant quel que soit V.

La mise en œuvre de cette méthode consiste dans la mesure de la différence des courants ioniques Δ li apparaissant quand Vr varie de Δ Vr pour différentes valeurs de V. La courbe Δ I i = f (V + Vr) permet de connaître avec précision la valeur du potentiel d'ionisation du gaz.

§ 3. Etude théorique de la relation Δ I i = f(V + Vr)

La forme de la courbe $\Delta I i = f (V + Vr)$ peut être prévue par la théorie. Le courant ionique $\Delta I i$ produit par des électrons ayant une énergie comprise entre U et $U + \Delta U$ est donnée par l'expression :

$$\Delta I i = A \cdot P(U) \cdot \Delta Ne$$

P (U) étant la probabilité d'ionisation des électrons d'énergie U, Δ Ne le nombre d'électrons ionisants et A une constante. Théoriquement et expérimentalement on a montré que pour une énergie proche de l'énergie d'ionisation Ui = eVi la probabilité d'ionisation est (8), (9) :

$$P(U) = a \cdot (U - Ui)^n$$

U — Ui étant l'énergie en excès sur l'énergie d'ionisation,
 n le degré d'ionisation, a une constante.

Nous supposerons dans cette étude théorique que la bande hachurée de la figure 7 est rectangulaire, donc que le nombre d'électrons représenté par cette bande est proportionnel à $\Delta V r$:

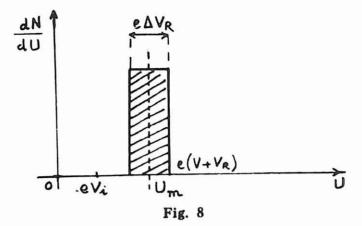
$$\Delta Ne = k \Delta Vr$$

Cette approximation est justifiée si la largeur e \Delta Vr est faible.

Ceci posé, trois cas sont à consídérer dans l'étude de l'ionisation produite par la bande d'électrons quasimonoénergétiques.

a)
$$V + Vr - \Delta Vr > Vi$$
.

Dans ce cas tous les électrons compris dans la bande sont ionisants, la limite inférieure en énergie de ces électrons étant encore supérieure à l'énergie d'ionisation.



L'énergie moyenne de ces électrons est

$$U_{m} = e \left(V + V_{r} - \frac{\Delta V_{r}}{2} \right)$$

L'application des formules donnant ΔIi et P (U) avec n=1 pour une ionisation simple donne :

$$\Delta I i = c \left[V + V_r - \frac{\Delta V_r}{2} - V_i \right] \Delta V_r$$
... avec
$$C = e \cdot A \cdot a \cdot K.$$

La courbe représentative Δ I i = f(V + V_r) pour V variable est une droite qui coupe l'axe des abscisses au point :

$$\Delta I i = 0$$
, $V + V_r = V_i + \frac{\Delta V_r}{2}$

b)
$$V + V_r - \Delta V_r < Vi < V + V_r$$
.

Une partie seulement des électrons ionise le gaz.

le nombre d'électrons ionisants est alors égal à :

$$\Delta N_{\bullet} = k (V + V_{r} - V_{i})$$

et l'énergie moyenne de ces électrons :

$$U_{m} = e \frac{V + V_{r} + Vi}{2}$$

$$\Delta I i = c \left[\frac{V + V_r + V_i}{2} - V_i \right] \left[V + V_r - V_i \right] \dots$$

$$\dots = \frac{c}{2} \left[V + V_r - V_i \right]^2$$

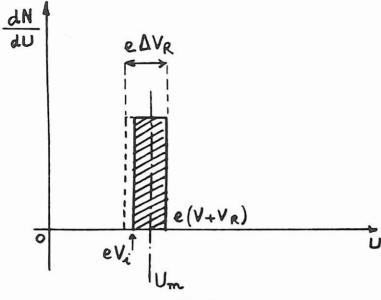
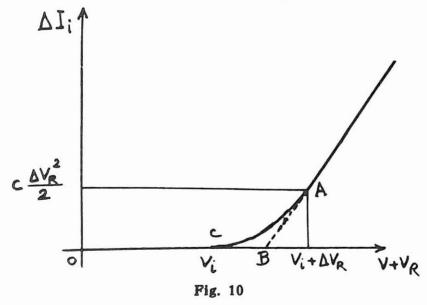


Fig. 9

La courbe représentative est une parabole. Il est facile de montrer que la droite trouvée plus haut et cette parabole se raccordent en un point A (figure 10).



l'extrapolation de la partie linéaire donne le point B d'abscisse :

$$\left(Vi + \frac{\Delta V_r}{2}\right)$$
c) $Vi \geqslant V + V_r$.

Aucun électron n'est ionisant Δ I i = 0.

§ 4. Résultats expérimentaux. Conclusion.

Nous avons déjà vu que l'utilisation de champs Ee et Ei pulsés supprimait la cause d'erreur a) et que l'utilisation d'une cathode à chauffage indirect ou d'une cathode à chauffage direct pulsé, supprimait la cause d'erreur b). L'emploi de faisceau d'électrons ionisants quasi monoénergétiques, d'après la méthode R. P. D. qui vient d'être décrite, permet alors d'obtenir des résultats expérimentaux en parfait accord avec la théoric. La courbe expérimentale obtenue qui traduit les variations de A I i en fonction de V + V, présente encore une « queue », mais celle-ci s'étend maintenant sur un intervalle étroit de 0,1 volt. De plus cette courbe a une forme bien définie à partir de laquelle on peut déterminer Vi avec précision soit en A, soit en B, soit en C. La « queue » de la courbe permet également une mesure de l'étalement en énergie des électrons ionisants.

Cette méthode donne des résultats en accord avec les valeurs spectroscopiques à 0,01 volt près (1). De plus, elle a permis pour la première fois de montrer que, pour des électrons quasi monoénergétiques, la probabilité d'ionisation simple était une fonction linéaire de l'énergie en excès sur l'énergie d'ionisation.

Wannier a développé une théorie (10) dans laquelle la probabilité est proportionnelle à la puissance 1,127 de l'énergie en excès. Mais la discrimination de Wannier ne s'applique que près du seuil d'ionisation, dans une région de 1 à 2 eV et dans cette région les différences introduites par les deux lois sont de l'ordre des erreurs expérimentales.

La méthode R. P. D. présente donc de très gros avantages: facilité de mise en œuvre dans la source d'ions d'un spectromètre de masse par addition d'une électrode, précision des résultats expérimentaux. Mais cette méthode présente quelques inconvénients.

a) La distribution en énergie des électrons à la sortie d'un filament à chauffage direct s'étend sur un intervalle de 2 à 3 ev, compte tenu de la loi de distribution en énergie et de la chute de potentiel le long de la cathode. Si on utilise une variation de potentiel retardateur de 0,1 volts, le courant électronique Δ I₀ qui correspond à la bande des électrons quasi-monoénergétiques est égal au quinzième environ du courant total émis par le filament (11). D'où une perte de sensibilité.

b) L'étroitesse de la distribution en énergie n'est vérifiée qu'indirectement par déduction sur les résultats expérimentaux.

(III). - LA METHODE DES SELECTEURS D'ENERGIE

§ 1. Généralités.

L'obtention d'un faisceau d'électrons dont les énergies sont réparties dans une bande étroite, en vue de l'ionisation d'un gaz, avait occupé les chercheurs bien avant 1951, date à laquelle Fox et ses collaborateurs publièrent leurs premiers travaux sur la méthode R. P. D. L'utilisation de sélecteurs magnétiques ou électrostatiques d'énergie (12) permet évidemment l'obtention de faisceaux d'électrons quasi-monoénergétiques. Ces dispositifs expérimentaux qui jouent le rôle de sélecteurs d'énergie ou de filtres de vitesses sont fort nombreux et nous n'avons pas l'intention d'en donner ici une énumération complète. Signalons par exemple le sélecteur électrostatique planparallèle utilisé par Hutchinson (12) et les sélecteurs d'énergie mettant en œuvre les propriétés focalisatrices bien connues d'un condensateur cylindrique d'ouverture

 $\frac{\pi}{\sqrt{2}}$ (méthode de Hugues et Rojansky). La mise en œuvre

de telles méthodes dont le principe est simple, complique beaucoup le dispositif expérimental de mesure des potentiels d'ionisation. Par contre ces sélecteurs d'énergie permettent l'utilisation de faisceaux électroniques qui, tout en ayant des énergies réparties dans des bandes étroites de l'ordre de 0,1 v, ont des intensités de 100 à 500 fois plus grandes que celle qui sont données par la méthode R. P. D. (7) (9). A titre d'exemple nous décrivons brièvement dans le paragraphe suivant la méthode utilisée par Hutchinson.

§ 2. Principe du sélecteur électrostatique plan-parallèle.

Une différence de potentiel Vo est appliquée entre deux plaques planes et parallèles P1 et P2. Si un faisceau d'électrons faisant l'angle Θ avec P2 pénètre dans l'espace compris entre les deux plaques par la fente S1, on montre que seuls les électrons ayant une énergie U bien déterminée peuvent sortir par la fente S2 (figure 11).

L'équation de la trajectoire est en effet :

$$y = -\frac{Vo}{d} \frac{e}{4U} \frac{x}{\cos \Theta} + x tg \Theta$$

S.C.E R.T., West Bengal Date 24, 2, 82. Acc. No. 2786.

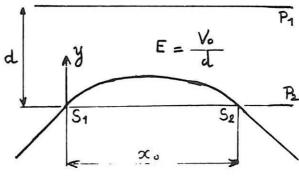


Fig. 11

Pour que les électrons d'énergie U sortent par la fente S₂ il faut que l'on ait:

$$x_0 = \frac{d}{Vo} \frac{2 U}{e} \sin 2 \Theta$$

avec $\Theta = \frac{\pi}{4}$ ef x = 2 d, la relation entre U et Vo

devient
$$U = V_0 e$$

Le sélecteur électrostatique donne donc à partir d'un faisceau d'électrons un autre faisceau d'électrons monoénergétiques. En réalité la distribution en énergie a la forme d'une courbe en cloche (figure 12.).

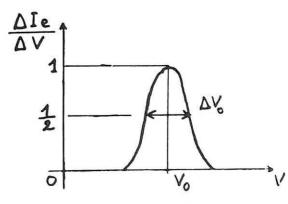
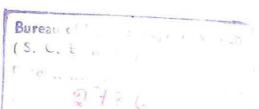


Fig. 12

La forme de cette courbe peut être déterminée expérimentalement. Par éxemple un deuxième sélecteur d'énergie (B) identique au précédent (A) reçoit le faisceau électro-



371.3 UNE



nique. On fait varier V, différence de potentiel appliquée entre les plaques de (B), autour de V_o. Pour chaque valeur de V on mesure le courant électronique Ie. En appliquant cette méthode Hutchinson (12) montre que l'étalement à mi-hauteur du faisceau électronique utilisé est 0,063 Volt.

Un calcul identique à celui qui a été fait dans le cas de la méthode R.P.D., compte tenu de cette nouvelle distribution en énergie, permet de prévoir théoriquement la forme de la courbe donnant les variations du courant ionique en fonction de l'énergie des électrons (9).

§ 3. Résultats expérimentaux.

L'utilisation d'un sélecteur d'énergie montre encore que le changement de pente de la courbe du potentiel apparent est directement lié à l'étalement en énergie des électrons ionisants. Les résultats obtenus sont en accord avec les résultats spectroscopiques à 0,02 eV près.

Conclusion

La methode de Franck et Hertz qui a été la première méthode électrique utilisée pour la détermination des potentiels d'ionisation n'a plus qu'un intérêt historique même sous la forme améliorée qui comporte l'emploi d'un gaz calibrateur.

La méthode R.P.D. qui met en œuvre des processus plus complexes, permet d'obtenir des résultats expérimentaux dont l'interprétation théorique repose sur des bases solides et qui sont en accord avec les résultats d'origine spectroscopique. Elle présente en outre l'avantage de ne pas introduire des dispositifs trop compliqués, puisqu'on trouve souvent dans la structure même des sources gazeuses d'ions des spectrographes de masse les diverses électrodes qui permettent de l'appliquer. La méthode R.P.D. nécessife cependant l'utilisation de champs pulsés produits par des générateurs d'impulsions à électronique rapide.

Les méthodes de filtres de vitesse ou de sélecteurs d'énergie imposent des dispositifs expérimentaux assez compliqués et qui doivent être spécialement construits. C'est là l'un des inconvénients de ces méthodes. Les résultats expérimentaux qu'elles permettent d'obtenir sont aussi précis que ceux obtenus par la méthode R.P.D.

En définitive les deux dernières méthodes permettent d'obtenir, par voie électrique, des valeurs de potentiels d'ionisation qui ne diffèrent que de 0,01 à 0,02 volt des valeurs obtenues par voie spectroscopique.

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AN EXPERIMENT ON MOLECULAR POLARITY

by

Th. Theimann, Lemgo

In molecules of the gaseous elements H_2 , Cl_2 , O_2 etc., as well as in the molecules CH_3 - CH_3 , $\operatorname{CH}_2 = \operatorname{CH}_2$, $\operatorname{CH} \equiv \operatorname{CH}$ etc., bonding electron pairs belong equally to the two atoms or the two radicals. Neither of the two partners attracts the bonding pair of electrons more strongly than the other. The molecules have a symmetrical structure; positive and negative charges have the same centre of action.

The same is true, too, for molecules of the type CH_4 , CCl_4 , CBr_4 etc. which have a tetrahedral structure. Here too the centre of the negative charges which form the bonding pairs of electrons is the same as that of the positive charges, i.e. the nucleus of the carbon atom.

All the above molecules are non-polar in contrast to polar molecules in which one of the partners exerts a stronger attraction upon the bonding pair of electrons than the other, as, for example, in ethylbromide CH₃-CH₂Br. The reason why the H₂O molecule has such a strong polarity is, of course, thoroughly dealt with already in school chemistry.

We can demonstrate that liquids consisting of polar molecules have common characteristics in an electric field which are absent in those consisting of non-polar molecules.

A burette is set up close to a metal ball $(1 - 1^{1/4})$ in diameter) in such a way that its outlet is about $\frac{1}{2}$ " away from the ball and above a line drawn horizontally through the centre of the ball. The ball is put on an insulated stand such as is used for electrostatic experiments, and is connected to the negative pole of a high-tension source of direct current at several thousand volts.

When water is released from the burette the stream is quite noticeably attracted towards the ball. The strength of the attraction increases in proportion to the voltage. This can be seen by connecting either

positive or negative poles to the ball. If a high-tension transformer is not available, the same if not even better results can be got by rubbing a polythene or hard rubber rod on a woollen cloth and holding it near the stream of water (both have a negative charge). This is very simple to do but, of course, the voltage cannot be varied.

How can we explain this experiment?

We know that the polar water molecules arrange themselves in the electrical field in such a way that they turn their positive ends towards the negatively charged ball. This re-arrangement of the molecules in the liquid causes the whole of the side of the stream facing the ball to be positively charged thus causing an electrostatic attraction.

On the other hand, a stream of ${\rm CCl}_4$, for example, is hardly attracted in this way at all. Here only a weak separation of the charges takes place and this is caused by induction.

In this way liquids can be examined to determine the polarity of their molecules, and the results agree with what we might expect. Thus we can prove that CHCl_3 and $\mathrm{CH}_2\mathrm{Cl}_2$ are polar, as are $\mathrm{CH}_3\mathrm{OH}$, $\mathrm{CH}_3\mathrm{CH}_2\mathrm{OH}$, we can prove that CHCl_3 (in the case of $\mathrm{CH}_2\mathrm{Cl}_2$ account must be $\mathrm{CH}_3\mathrm{COOH}$, and $\mathrm{CH}_3\mathrm{COCH}_3$ (in the case of $\mathrm{CH}_2\mathrm{Cl}_2$ account must be taken of the spatial arrangement of the atoms attached to the carbon atom to see the polar nature of the molecules). $\mathrm{C}_6\mathrm{H}_14$, $\mathrm{C}_7\mathrm{H}_16$ and $\mathrm{C}_6\mathrm{H}_6$ are non-polar. Car petrol contains polar molecules.

This experiment can, of course, be developed further to yield quantitative results.

SNOW AND HYDROGEN BONDS

by Eric Cappelin Östra Real Stockholm, Sweden

C.P. Snow has diagnosed one of the social illnesses of this century. As a research scientist in Cambridge and a fiction writer he has oscillated between what he calls "the two cultures". He says that humanists and scientists are "two groups - comparable in intelligence, identical in race, not particularly different in social roots with about the same incomes - that have practically cut off communication".

The culture of the ancients was not divided. Lucretius (99 - 55 B.C.), the Roman protagonist of epicurean philosophy, could write "On the Nature of Things" in hexameters and define an element thus:

For must needs be there something immutable left to

survive, lest

All things wholly revert unto naught.....

(Lucretius, "On the Nature of Things". A translation in the metre of the original by L.L. Johnson, 1964, Riband Books, Horsham, Sussex.)

Elements had been discussed already in the sixth century B.C. in the greek city of Miletos on the west coast of Asia Minor. Thales, the merchant, taught that "the beginning of everything is water" - which is common and wet. Anaximander, the politician, on the contrary strongly held that the element had nothing to show our five senses. The "wet" and "flowing" characteristics disappear when water freezes but the basic substance remains.

Anaximenes, the third Milesian philosopher, thought that "the element was one and infinite but did not say like Anaximander that it was indefinite but that it was definite because he said it was air." Different substances came into being by condensation or rarefaction of "air". But in Ephesos Herakleitos taught the opposite, namely that air and everything else was condensed "fire".

The chemistry of the Greeks generalized the transformations of water. Solid matter was ice, liquids water, gas steam, and fire surely superheated steam. To hold the theory of one basic principle, e.g. of one element, is to be a monist. The pluralist Empedokles had four: earth, water, air and fire. His theory of four elements came into the scholasticism of the Middle Ages via Aristotle and was accepted into fairly recent times. Priestley, one of the discoverers of oxygen, all his life he died in 1804 - regarded water as an element. And so did Cavendish, the discoverer of hydrogen, who died in 1810.

"A History of Greek Philosophy" by W.K.C. Guthrie (Vol. I, Cambridge University Press, 1962) has received good criticism. In the preface (p. ix) one reads: "Far from being a pioneer study, this history deals with a subject of which almost every detail has been minutely worked over many times". As the transformations of water are common denominators for all the ancient philosophers in their speculations on elements, we shall scrutinise that detail.

Guthrie has objections to what P. M. Cornford (Principium Sapientiae p. 6) has written: "Anaximenes affords another instance of a hypothesis which no one tested. He held that differences of heat and cold can be reduced to differences of density; steam is hotter and less dense than water, water hotter and less dense than ice. If that is so, a given quantity of water ought to fill less space when frozen. Had Anaximenes set a jar full of water outside his door on a frosty night and found it split in the morning, he might have found out that ice fills more space than water and revised his theory."

To this Guthrie adds: "This result would certainly have puzzled him, but the fact remains that his general theory was right, and if he had performed the experiment and based any generalization on the results, it would only have led him into error. In general, bodies do of course expand as their temperature rises, and contract as it falls, a principle which makes the thermometer possible. Water itself expands as it is heated, and

contracts as it is cooled, until it reaches a temperature of 39°F (4°C). Then for some reason as it becomes colder and passes freezing point it ceases to contract and begins to expand. This exception to the otherwise universal truth that bodies expand by increase of temperature is still unexplained, that is, scientists have still failed to relate it to any general law. It is perhaps hardly fair to Anaximenes to blame him if, having correctly divined an almost universal truth, he failed to observe the single exception which has hitherto baffled the efforts of scientists to explain it."

This is nonsense. In Cambridge many students know that the properties of water and ice stem from the hydrogen bonds between the H₂O-molecules. But Professor Guthrie seems to have contented himself with looking up "Water" in the Encyclopaedia Britannica, to which he himself has contributed. Hydrogen bonds are unfortunately not mentioned there. They are subject to intense research, which does not easily lend itself to popularisation. But from the following it should be evident that quite a lot is known about the internal behaviour of water even if small differences as regards angles, distances and other things still have to be clarified.

H₂O behaves strangely. But ice contracts when cooled down just like other solids. Nevertheless, ice occupies a larger volume than the water formed on its melting - ice floats. Pig - iron behaves in the same way and so do the metals bismuth and gallium which also contract on melting.

Towards the end of the nineteenth century one started to suspect that water was a mixture of molecules different in size, the mutual proportions of which varied with the temperature. Röntgen wrote in 1892 (three years before the discovery of the radiation that made his name famous): "The molecules of the first kind, the ones we also call ice molecules because we attribute to them some of the characteristics of ice, turn on heating into molecules of the second kind; but if heat is removed, a corresponding number of ice molecules are reformed. We may regard the water, if not under-cooled, as a completely saturated solution of ice molecules, which is more concentrated, the lower the temperature".

Hydrogen bonds between molecules are considerably weaker than the bonds between the atoms in a molecule. They were discovered in 1912. In 1933 J.D. Bernal and R.H. Fowler advanced a theory that on the whole still holds for ice and water.

There are no hydrogen bonds in water vapour. The molecules H-O-H are bent. In the vapour, the angle hydrogen-oxygen-hydrogen is 104.5° and the distance from H- to -O- is 0.96 Å. The hydrogen 'legs' have a surplus of positive electricity while the -O- atom gets two negative spots (2e and 2e) at the opposite side.

When it is snowing or hailing the cold in the atmosphere slows down the thermal movement of the water molecules so that their positive hydrogens find a resting place by forming hydrogen bonds with the negatively charged oxygens of other hydrogen molecules. With the negatively charged oxygens of other hydrogen molecules. The pattern is obvious - one molecule will be surrounded by four others. When the molecule is caught, its angle is forced out from others. When the molecule is caught, its angle is forced out from 104.5° to 109.5° and H-O-H is inserted as a tetrahedral building element in the ice structure. Every hydrogen atom finds itself between two oxygen atoms. Conversely, every oxygen is surrounded by four hydrogens. Two of these are so close to the oxygen, 1.0 Å, that distinct water molecules can still be regarded as existing in the solid phase. The two others are more than 1.7 Å away - hydrogen bond distance - and belong to two other water molecules. The ice structure has been determined by X-ray diffraction.

If water freezes quickly a conglomerate of ice crystals is formed. In the clean water of our lakes in Lapland it happens that crystallisation starts from one point so that the lake is covered by one giant crystal - so called blue ice. Only Canada with its black ice can compete with us for the world record. Ice is a semi-conductor. A small concentration, for instance, of ammonia disturbs the crystal structure and gives ice transistor properties. Such ice can be used as a rectifier.

When ice melts, the volume gets smaller, as when a card house is overturned. Melting does not involve a total collapse of the ice structure, however; a certain co-ordination remains between each H_oO unit and its neighbours. The liquid is a system of hydrogen bonds, flexible of course - how else would water be able to flow? At constant temperature, only a rearrangement of a fixed number of hydrogen bonds occurs - as many are broken as formed. the water structure continues to collapse while, on the other hand, the increased thermal motion tends to expand the volume of the liquid. Up to + 4°C, shrinking prevails. On heating, a substantial part of the added energy is used for the breaking of hydrogen bonds and does not contribute to the increase in thermal energy, i.e. temperature. This is why water has such a high specific heat. Consequently, water is also very difficult to cool; it is the outstanding heat accumulator in nature. Much heat is absorbed when ice at 0°C is transformed into water at 0°C and still more when water evaporates.

By considering the close relatives of water according to the periodic system - the strongly smelling gases hydrogen sulphide, hydrogen selenide and hydrogen telluride - it is possible to figure out that H-O-H with simple molecules would not freeze until -100°C and would boil at -80°C. The earth would then be empty and waste, as life itself depends on hydrogen bonds. Thales would never have existed.

The Use of Models in the Teaching of Chemistry

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1. Why use Models?

The use of the concepts of relative size, geometrical shape and structure in relation to the study of chemistry is an essential feature of a modern approach to the subject. We base our explanations of the chemical properties of many species of atoms or ions on their relative sizes in addition to other factors. The reactivity of a molecule or the way in which a reaction may occur is often determined by the geometry of the molecules or ions concerned.

Unfortunately we cannot use pictures of actual molecules or ions, nor can we enable the pupils to see real particles of atomic dimensions. However to leave these particles as purely abstract concepts would make the understanding of chemistry extremely difficult for all but the exceptional pupil. It must be clearly understood that a model is a simplification, often a gross over-simplification of something which has a complexity which man is still trying to unravel, e.g. in the case of the atomic nucleus. A model can merely represent one or two features of the units being studied. cannot have an 'accurate' representation of atoms for the pupils, so we must make do with an approximate representation of some features of the atom and of molecules.

A difficult concept can only be explained to the limits of a student's experience. If it can be made clear by resorting to simple models which, although they cannot depict the true complexities of reality, do not distort reality and do help the student to detect some reasonableness in natural law, then there can be no valid argument against the use of such models. If a student can look at an assemblage of polystyrene spheres identified as the atom of an element, and from it know correctly that the atom has a certain relative size compared to other atoms, that it has the capacity to form a specific number of covalent bonds and why it has that capacity that these bonds have special directional characteristics and why, that it can act as an electron donor or acceptor and why, that it has a certain relative attraction for valence electrons that will result in bond

polarity in a certain direction in combination with different atoms, of a direction and an approximate extent that could be immediately determined by inspection of a similar model of the other atom, and in addition to all this, if he can with the help of a little supplementary information predict accurately from these models, many of the physical and chemical properties of the compounds or other aggregates formed by these atoms, then why not use such models.

In presenting models, it must always be made perfectly clear to students that real atoms and molecules do not bear a close resemblance to the models, except to the relative extent to which they occupy space. Atoms are dynamic systems, elctrons are in effect more cloudlike, not stationary particles, and the models portray only a few or even only one of the real qualities of the particles concerned, rather than give a true physical picture of the particle.

In School Certificate work, we will not be greatly concerned with the more sophisticated uses to which models can be put, but nevertheless much of what has been said above is applicable to our work.

In developing countries there is an added need to provide some concrete representation of the abstract concepts of size and shape in relation to atoms and molecules. It is well known in educational circles that the child in a developing country is in a much poorer environmental situation as compared with his brethren in more developed countries. He is not exposed to the mass educative media of Radio and even more important Television, to the same extent, as children in Britain or America. He does not have the same wide variety of literature, pictorial or otherwise, on which to feed his developing intellect. It is not surprising therefore that young African children are found to be lacking in a proper understanding of such concepts as perspective in drawings, the interpretation of line diagrams in terms of three dimensional objects, etc. This being the case, it gives an added reason for an extensive use of visual aids of all kinds in our teaching. It is probably true to say that, apart from the Periodic Table, a series of atomic and molecular models is the most valuable educational aid a chemistry teacher can have in any country, let alone

a developing one.

In the context of the school certificate syllabus, how can one explain the hardness of a diamond, the lubricating powers of graphite, the hardness and solidity of sodium chloride in its crystalline form at room temperature, the crystalline forms of innumerable compounds, the allotropy of sulphur, etc., without recourse to illustrations involving models?

The acquisition of a set of atomic and molecular models, and of materials for the improvisation and construction of these models by the teacher and by the pupils, is an absolute necessity for the teaching of Chemistry at any level.

2. Types of Models

The properties which we usually require our models to represent are the relative sizes of atoms or ions either singly or in combination with other atoms or ions, the spatial arrangement of the particles in the ionic lattices or in molecules, the geometrical 'shape' of the molecule or unit of the substance, and possibly additional features such as the electronegativity of the particles concerned, and the outer shell electronic configuration.

A number of different criteria of the 'size' of particle exist. They are IONIC RADIUS, COVALENT RADIUS, and VAN Der WAALS RADIUS. With Ionic models the choice is obvious and Ionic radii for many species are well known. In the case of covalent molecules however some difficulty arises. Within a molecule the linkages are covalent and naturally one would wish to use models which represent the relative covalent bond lengths. However, in extended crystal lattices of covalent molecules, the inter-molecular distances are determined largely by Van Der Waals forces and it is usual to the Van Der Waals radii to determine the intermolecular distances. Both covalent and Van Der Waals radii can be determined, but only the covalent radii can be easily obtained, from bond length measurements. The Van Der Waals radii are vague and uncertain and depend on conditions which

are often difficult to evaluate accurately and different radii of this kind may appear in the same molecular lattice e.g. in CCl₄₁, two chlorine atoms of different molecules appear to approach no closer than twice the accepted Van Der Waals radius, but two chlorine atoms in the same molecule are much closer together than this distance, but are still separated by non-bonding forces. For these reasons therefore it is usual to build models based on covalent radii, and to remember that inter-molecular interactions require much larger distances.

The question of chemical reaction also favours the use of covalent radii. Although Van Der Waals radii give a measure of the closest non-bonded approach of molecules, chemical reaction presumably requires a much closer approach than this and covalent radii should give a more realistic measure of this factor. For this reason most systems of models in which relative size factors are involved, use where appropriate the covalent radii of the atoms concerned.

There are many types of actual models, some of which are intended to represent only one of the above properties of the molecules or ionic units they are portraying.

(a) Elements

The simplest form of atomic model. is a sphere with its size chosen to fit into a suitable scale depending on the intended usage of the models. For teacher demonstration purposes the scale should be larger than when the models are to be constructed by the pupils e.g. 1.5 inches per Angstrom unit for Teacher Demonstration purposes, and I inch per Angstrom unit for pupils constructional work. Any scale may be chosen however to suit the range of materials available. With such models it is possible to represent, e.g., relative sizes of atoms and the corresponding ions down a group in the Periodic Table, and, by linking the models to the Periodic Table and, painting according to an appropriate colour scheme, it is also possible to show electronegativities and the relation of this property to the position of an element in the table.

Where covalent molecules are formed by the elements, the spheres would normally represent the covalent radii of the element and they should be joined together in units representing the molecule of the element

where appropriate, e.g. Phosphorus, a tetrahedral arrangement of 4 phosphorus atoms and Sulphur, a puckered octagonal arrangement of 8 sulphur atoms. It must be remembered that multiple bonding shortens the covalent radius, e.g. 0-0 is longer than 0 = 0.

The representation of extended metal lattices is based normally on the idea that a metal unit can be regarded as a collection of cations embedded in and held together by an electrostatic glue of mobile electrons. This rather crude picture gives rise to three distinct packing arrangements, hexagonal close packed, body centred cubic and face centred cubic. There is no obvious face centred cubic. relationship between atomic structure and the crystal structure of the metals concerned. Examples are as follows:

Li, Na, K, Rb Body Centred Cubic Cs, Bi, Fe.

Cubic Close Packed (Face Ca, Sr, Fe, Co, Ni, Cu. Centred Cubic)

Hexagonal Close Packed Be, Sc, Ti, Co, Ni, Zn, Cd.

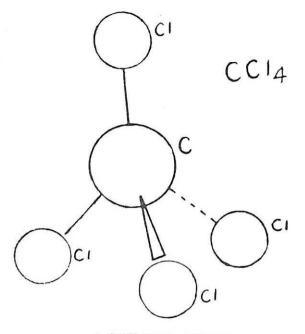
These structures can be built up from spheres of the appropriate size packed together in the appropriate geometrical In a body centred cubic lattice each atom is surrounded by eight closest neighbours in the form of a cube with itself at the centre of the cube, and by six more atoms a little further distant at the centres of the six adjacent cubes.

The face centred cubic and hexagonal close packing systems arise from different combinations of the same basic pattern. In each a central atom is surrounded by a plane hexagon of six more atoms. Then each solid hexagon has a triangle of atoms above and below, making 12 nearest neighbours in all. The difference lies in the orientation of the two triangles with respect to each other. If they point in the same direction, the structure is hexagonal, if they point in opposite directions, the structure if face centred cubic.

(b) Compounds

It is possible to represent compounds in two basic ways. In one, the atom or ion is indicated by a sphere of standard size and the bonds or total interionic distances are represented by a metal rod or spring of some kind. The lengths of these connectors may or may not represent relative bond lengths or relative interionic distances. In the other, the molecules or ionic lattices are built of spheres which represent the relative covalent or ionic radii of the particle concerned. The spheres are attached to one another at the appropriate angles to form the molecule or extended ionic lattice. Both types of model have their uses. In the first type an open network is created and the overall geometry of the system is clearly discerned. In the second type, which are sometimes referred to as space-filling models. a truer representation of the spatial factors involved in the molecular structure is obtained and this can be of considerable importance in, e.g., determining the vulnerability of a covalent molecule to attack by a reactive species at given points throughout the molecule. A useful way of helping pupils to get the 'fcel' of 3.D. structures is to allow them to build skeletal models of the regular solids-Tetrahedron, Octehedron, etc.

Models of both types may be purchased or made. Griffin & George market a set of ball and spring models, a simple set of which costs £9. 10s., a more senor set is available costing £17. 4s. (1966 catalogue). Individual plystyrene spheres may purchased from a number of sources -Griffin and George market them under the name of "POLYZOTE SPHERES" at prices ranging from 13/- to 25/- per hundred depending on the diameter of the sphere. They may also be obtained from Elford Plastics Ltd., Brookfield Works, Wood St., Elland, Yorks, U.K. at similar prices NAAFCO (these are the U.K. prices). would presumably be prepared to obtain supplies at some extra cost. These spheres can be used to make any of the space filling models above, but they require painting. glueing and sometimes cutting, where multiple bonds are to be represented. A more expensive set of space-filling models is marketed by Griffin and George as "COUR-TAULD ATOMIC MODELS". These ready made plastic models have a special linkage system which allows some flexibility which is not available with the polystyrene spheres. A very small set of these costs £7: 19s: 6d., but the most useful set costs £31: 9s: 9d. These are for representing covalent molecules only. Other sets of models are available for representing ionic



A SKELETAL MODEL

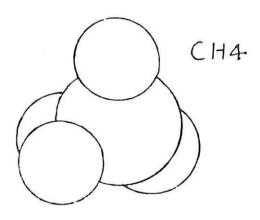
Figure 1

structures notably those manufactured by Catalin Ltd.

3. Making Models

Apart from the basic data on molecular structure, atomic and ionic sizes and covalent radii, which may be obtained by reference to suitable textbooks on the subject, probably the best single book that has appeared is "Teaching Chemistry with Models" by R. T. Sanderson, published by Van Nostrand at 45/-. The models in the book are made from polystyrene spheres, but the data is applicable to other materials.

Skeletal models may be manufactured either on a temporary or a permanent basis using a number of materials. simplest materials are plasticine, or even local clay, and some sort of rigid or semirigid connector e.g. match-sticks, cocktail sticks (the plastic variety are quite strong), or best of all if a fairly flexible system is required, extendable curtain wire. last connector has the advantage that it can be cut to various lengths to represent the appropriate ionic or covalent radii etc. If curtain wire connectors are used, plasticine will probably be too dense a substance to use for other than very small molecules or atomic or ionic aggregates and wooden 'atoms' or 'ions' with holes drilled at the



A SPACE FILLING MODEL
Figure 2

appropriate angles should be used. Ideally a spherical 'atom' representation should be used, but if the purpose of the model is simply to show molecular geometry, there is no reason why small cubes should not be used, provided it is pointed out that they merely indicate the centres of the 'atoms' or 'ions' that they are meant to represent. Most of these materials can be obtained locally. An interesting and versatile improvisation of atomic and molecular models of this type, which uses simply the position of joining of the various bonds or connecting links to represent the positions of the centres of the particles, is given in School Science Review No. 163 June 1966 by Hobson and Platts which uses pipe cleaners (or pieces of wire with cotton wool twisted around them) and ordinary milk straws (soda straws). The straws are cut to the appropriate lengths to represent the bonds or inter-ionic distances. Quite extended models can be made using this system, which is extremely cheap. Space filling models are more difficult to make, but a selection of them are well worth making despite the effort. Again the simplest ones can be made from different colour plasticines, using one colour per particulate species.

The polystyrene spheres are probably the best materials for making these in schools. These are white, but may be painted by a number of techniques, dipping in car enamel of the appropriate colour, or by making a mixture of tempera colours in a rapid drying vanish as solvent. This latter method tends to soften the surface of the polystrene which then hardens after absorbing the paint particles giving a good non-flake surface colour. A suitable colour scheme for representing electronegativities is appended at the end of this paper. Spheres of wood would be equally suitable for these purposes but are not easily obtainable here. Polystyrene spheres may be fixed together by inserting short lengths of wire, or by Polystyrene cement glue gluing, or both. should not be used.

A necessary and extremely useful tool for the construction of models suing spheres in either type of model is a template giving the angels at which various types of bond are arranged around the sphere. angles are then used to determine the positions for drilling holes to receive connectors in skeletal models, or to determine the points of contacts of spheres in space filling models, where tangential contact is used to represent a single bond, and interpenetration of varying degrees is used to represent A suitable template multiple bonding. can be made from stiff white card by cutting out semicircles of various diameters from 3"-3" and marking around the circumference of the semicircle various important angles necessary for the determination of bond positions.

The reasons for the particular bond angles are often a mystery to school certificate pupils, and any explanation of this in terms of hybridisation or Molecular Orbital Theory is obviously inappropriate at this level. Nevertheless pupils will at this level appreciate that like electrostatic charges repel one another, and also that two electrons may either form a bond (covalent or co-

ordinate) or may form a lone pair. If the point is made that respective bonding and non-bonding pairs of electrons repel one another by electrostatic forces then a suitable analogy of the orientation of various numbers of bonds in space can be given using inflated ballons of different colours. One colour may be chosen to represent bonding pairs and another to represent non-bonding pairs.

In this way the angularity of water, the trigonal pyramidal shape of ammonia and many other simple structures can easily be displayed. It also helps the pupil to appreciate the stable octet electronic patterns in many of the simple compounds he meets. The basic principle involved is that the number of bonding and non-bonding pairs of electrons will orient themselves in three dimensional space so as to be as far apart from each other as possible and so to minimise the repulsive forces. This crude approximation serves very well for School Certificate purposes.

4. Specific Instructions

Here are a few specific instructions for model construction. Many other models

are possible and are easily constructed from the data available in the literature.

(i) (a) Diamond

Bond length 1-54°. (The bond length is the distance between the centres of the atoms joined by the bond. Four equivalent bonds at 109° 28' to each other — this is the regular tetrahedral angle. Two possible extended structures can occur one of which is the diamond structure and the other, unknown in carbon, occurs in the Wurtzite lattice. (found in Zinc Sulphide).

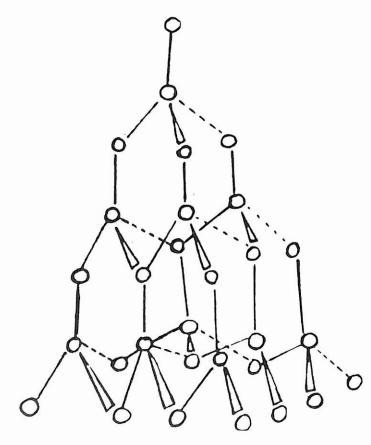


Figure 4

(b) Graphite

Bond length in each planar layer = 1.42\hat{\lambda}

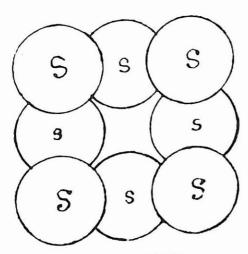
Bond Angles in each planar layer = 120\circ\.

Inter layer distance = 3.35\hat{\lambda}.

The layers are arranged so that a carbon of one layer is centred over a hole in the next layer: this leads to an ABAB type structure, another modification is possible giving ABC ABC patterns, both occur in graphite.

(ii) Phosphorus

P4 A tetrahedral arrangement of four atoms, with an atom at each vertex of the tetrahedron. Bond length 2.1%.



PLANE VIEW

Figure 5

(iv) Carbon Dioxide

This molecule is linear (remember multiple bonding affects the geometry) Bond length = 1.15 $^{\circ}_{A}$ and the carbon atom is in the middle between the two oxygen atoms.

(v) Carbonate Ion

This ion is planer with three equivalent oxygen atoms around a central carbon atom. Bond length = 1.31% and bond angles are all 120°.

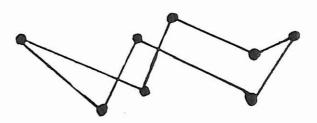
(vi) Water

This is an angular molecule. Bond lengths = 1.17%.

The lone pairs may be represented by putting very small polystyrene spheres on the oxygen atom at the appropriate position.

(iii) Sulphur

S8. All the bond angles are 105°. A total of eight atoms form a puckered octagonal pattern which can be regarded as one square of four atoms on top of the other, sekwed by 45°.



SKELETAL MODEL

Figure 6

(vii) Ammonia

This is a trigonal pyramidal structure. Bond lengths 1.12°_{N} H-N-H Bond angles = 107° .

(viii) Methane

A tetrahedral structure. Bond lengths = 1.14°. H-C-H Bond angles = 109° 28'.

(ix) Ethylene

A planar molecule. C=C Bond length = 1.34°. Attach four hydrongen atoms in one plane so that all the angles in the plane are 120°.

(x) Acetlylene

A linear molecule. C=C bond length = 1.20 $^{\circ}$. Attach a hydrogen atom at end of the molecule.

xi) Benzene

This is a planar molecule with C-C bond lengths = 1.39% forming a regular hexagon of 6 carbon atoms with the C-C-C angle = 120°. Attach one hydrogen atom to each carbon at 120° for the H-C-C angles.

(5) Colours for Representing Electronegativity and Partial Charge (After Sanderson — p. 145).

Electronegativity	Partial Charge	Colour	Approximate Mix, Dry Tempera, by Volume
0.49 — 0.69	0.60 or higher	read	R(red)
0.70 - 0.90	0.50 - 0.59	Orange-red	2-0/5R
0.91 - 1.11	0.43 - 0.49		3-0/4R
1.12 — 1.32	0.36 - 0.42	red-orange	2-0/1R
1.33 — 1.53	0.30 - 0.359		6-0/1R
1.54 — 1.74	0.25 - 0.299	orange	0 (orange)
1.75 - 1.95	0.20 - 0.249		1Y/5-0
1.96 - 2.16	0.15 - 0.199	yellow-orange	1Y/1-0
2.17 - 2.37	0.10 - 0.149		2Y/1-0
2.38 - 2.58	0.07 - 0.099	orange-yellow	4Y/1-0
2.59 - 2.79	0.04 - 0.069		6Y/1-0
2.80 — 3.00	0.02 - 0.039		24Y/1-0
3.01 — 3.21	0 to + 0.019	yellow	Y (yellow)
3.22 - 3.42	-0.02 to -0.039	Greenish yellow	24Y/1G
3.43 - 3.63	-0.04 to -0.069		13Y/1G
3.64 - 3.84	-0.07 to -0.099		6Y/1G
3.85 — 4.05	-0.10 to -0.140	yellow-green	5Y/2G
4.06 — 4.26	-0.15 to -0.199		4Y/3G
4.27 — 4.47	-0.20 to -0.249		3Y/4G
4.48 — 4.68	-0.25 to -0.299	green	G (green)
4.69 — 4.89	-0.30 to -0.359		5G/1B
4.90 — 5.10	-0.36 to -0.429	blue-green	5G/2B
5.11 — 5.31	-0.43 to -0.499		4G/3B
5.32— 5.52	-0.50 to -0.599		3G/5B
5.53 — 5.75	-0.60 or higher	blue	B (blue)

Milk-straw molecular models

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INTRODUCTION

This article attempts to show how milk straws and pipe cleaners, which are both cheap and readily available materials, may be exploited by the teacher and student to assist in the understanding of some structural aspects of chemistry. Applications to geometry are also implicit in our descriptions and certain uses for biology and engineering classes have been observed. Once the simple construction techniques have been mastered, a large number of applications arise. On the one hand they are useful to the expositions and demonstrations of the teacher, whilst on the other, the pupil at the concreteempirical stage of the learning process can learn much by building some structures for himself.

USES

Several uses are illustrated by photographs; but a start, in order to practise the technique, can be made by making polygons. It is then a simple matter to construct a set of the common regular polyhedra (the Platonic solids) for permanent display. In a similar way, models to illustrate the shape of the unit cell for each of the seven crystal systems may be made. These models can be distorted quite easily so that by pushing the model from an appropriate direction one system may be converted into another. For example, cubic can be transformed into rhombohedral, and orthorhombic into monoclinic first, then into triclinic. Obviously the Bravais lattices, e.g. face-centred and bodycentred cubes, etc., are quite feasible and a complete set could be made if

Models of chemical structures made by this method have a piece of straw cut to an appropriate length to represent the bond length (inter-nuclear distance) between atoms. Angles between bonds are determined by bends in the pipe-cleaner connectors. In this respect they resemble, superficially, the Dreiding structure models [1, 2, 3, 4, 5] designed for organic molecular structures. This particular type of structure model, which might be regarded as a 'ball and spoke' model, minus the balls, is particularly useful when an idea of the molecular framework is required. Also the conformational changes which occur when rotation about bonds takes place in a large structure are easily seen. In a large structure model of this type, the interior visibility is unsurpassed by any other type or system of modelling material. Simple structures are quickly made (e.g. hydrocarbons, aliphatic or aromatic) and the symmetry or asymmetry seen thus leading on to demonstrations of isomerism. The technique is so rapid that a model of the α -helix of a polypeptide was built in about two hours. This particular model contained fifteen amino acid residues. Models of sugar molecules, cellulose, polycyclic hydrocarbons, and polymers found in plastics, have all been made quickly and at low cost. The technique can also be applied to construct models of some giant structures studied in inorganic chemistry.

In all fairness it must be stated that these models are not so accurate or so robust as the commercially available types now made from stainless steel, wire or plastics, but if they are handled carefully, they could prove very useful to teachers and students. We are of the opinion that the advantages of low cost and availability far outweigh these disadvantages.

Other applications of the technique which have been tried were in biology and engineering. One pupil constructed a series of models showing the evolution of the pentadactyl limb through wings of pterodactyl, bat and bird. There is an obvious extension of this work to other skeleton structures. Frame structures of the engineer, e.g. cantilevers, may be built also.

CONSTRUCTIONAL DETAILS

Milk straws cost about one shilling for a hundred and one can buy plain white ones and some with coloured diagonal stripes, there being six different colours. A good start can be made with one box of straws and about a dozen packets of pipe cleaners (usually twopence a packet). For chemical structures we found that a scale of one inch per ångström unit was both convenient and economical. A scale of two inches per ångström or even larger is quite feasible where structures have to be used in large lecture rooms. One centimetre per ångström proved too small a scale to be useful.

The straws are cut to length with scissors and once one piece has been measured out accurately, using a ruler, the others can be cut by holding the measured pieces in the palm of the hand, the little finger acting as a stop. Two methods of connecting with pipe cleaners have been developed, one permanent, the other not. For class use, lengths of pipe cleaner about one inch long are cut, bent to an appropriate angle and stored in a box. One of these pieces is necessary for each angle between the straws. For example, a tetrahedral arrangement representing the bonds from a carbon atom needs four such pieces, whilst the corner of a cube requires three (Fig. 1). Experience

has shown that although one pipe cleaner will hold two straws together, a straw will accept up to three of these connectors and that, with two or three of them in the straw, the connection is firmer, yet the property of free rotation is still preserved. A box containing three dozen connectors (1 inch) and some lengths of straws (11 and 1 inch long) forms the basis of a pupil kit for

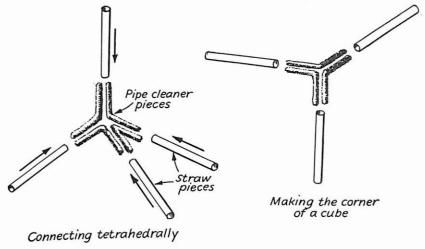
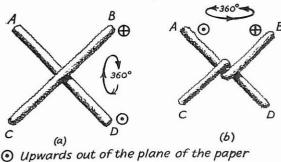


Fig. 1

constructing organic molecular models. In the second or more permanent method of using connectors, two or three pieces of pipe cleaner are twisted together to form a firm knot. Then the ends are arranged spatially to the correct angles. A method of making a knot quickly, and one which will not slip apart later, is shown in Fig. 2. In the case of planar bonds (carbonyl, amine, etc.) two of the ends are placed in the same milk straw. When the structure has been assembled, the angles and symmetry are finally adjusted by the use of hand and eye.



Downwards

Fig. 2. 1. Place two pieces of pipe cleaner at right angles as shown in (a). 2. Hold ends A and C in left hand, twist B and D through 360° with right hand (B downwards, D upwards). This gives (b). 3. Hold ends C and D firmly in left hand; twist A and B through 360°, A coming upwards and B downwards. 4. Adjust to correct angles between

Striped straws are useful to emphasize differences in length such as the values of a, b, c, in the crystal systems. A limited personal system of colour coding could be devised also for C—C, C—N, C—H bonds but we have found it best to use plain straws for organic models and then some colour is painted, according to accepted convention, where the bonds join. Ideally the lengths of colour along the straw could be the same as the covalent radii of the atoms forming the bond, though we doubt whether the extra trouble involved is necessary. However, some colour is extremely valuable in helping one to see the relative positions and types of atoms in the structure. As the straws are waxed, water paint is not suitable and an oil-based paint is required. We have used ready-mixed poster paint.

SOME NOTES ON THE CONSTRUCTION OF PARTICULAR EXAMPLES

1. In the diamond structure, the straws are cut to a length of 1.5 in (C-C = 1.54 Å). For graphite the lengths are 1.4 in (C-C = 1.42 Å) and the layers are separated by sheets of thin transparent plastic made up in the form of a box and held together by impact adhesive (Plate 3).

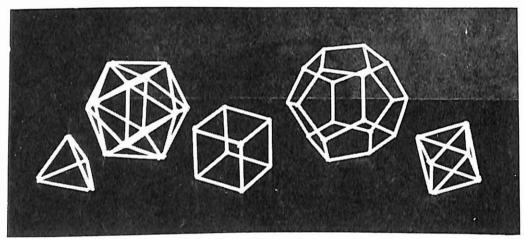


Plate I. Regular Polyhedra. L.-R.: Tetrahedron, icosahedron, cube, dodecahedron, octahedron

2. The polyhedra have edges of from 1 in to 4 in and the edge of the dodecahedron is 2 in, the whole structure then being about the size of a small football (Plate 1).

3. The \alpha-helix of a polypeptide contains 15 amino acid residues

H H $\begin{array}{c|c}
 & | & | \\
 & | & | \\
 & -C-C-N- \text{ and there are } 3.6 \text{ residues per turn of the helix. Radical } R \text{ is} \\
 & | & | & | \\
 & O & R
\end{array}$

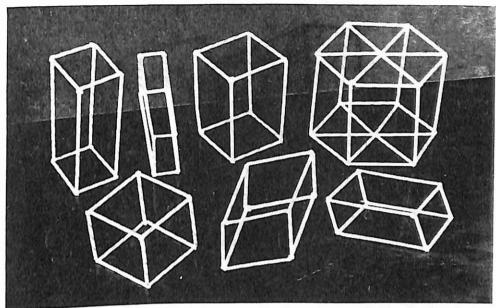


Plate 2. Unit cells of the seven crystal systems. L.-R. front row: Cubic, rhombohedral, triclinic. L.-R. back row: Monoclinic, orthorhombic, tetragonal, hexagonal

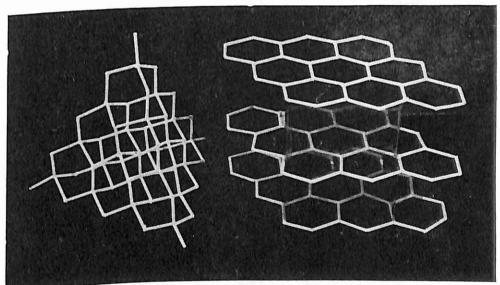


Plate 3. Diamond and graphite

omitted and it should be remembered that the grouping —C—N—C—C—
$$\parallel$$

which repeats round the coil is a planar arrangement. The distance between nitrogen and oxygen atoms, via hydrogen bonds, is 2.79 Å. It is these hydrogen bonds which are said to hold adjacent coils together in the helix. Scale

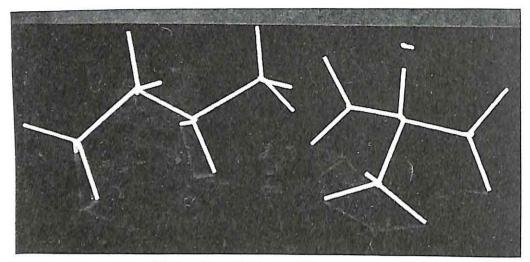


Plate 4. L.: n-butane, and R.: iso-butane

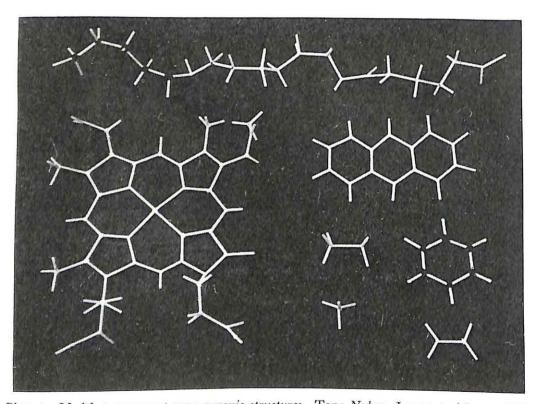


Plate 5. Models to represent some organic structures. Top: Nylon. L.: part of haemoglobin. R.: Anthracene, ethane, benzene, methane, and ethylene

used was I in per Å and the whole structure is about two feet long (Plate 7).

4. Simple hydrocarbons on a 1 in/Å scale, e.g. methane and ethylene (Plate 5), etc., are rather small and scaling could be doubled, but anthracene is about 9 in × 4 in. A three-glucose-unit cellulose chain is about 18 in long.

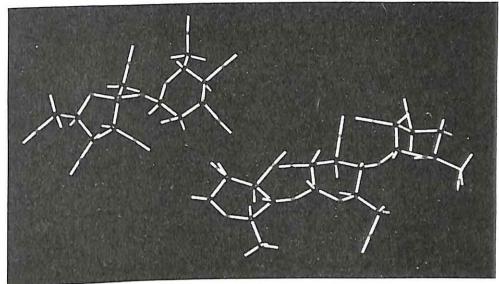
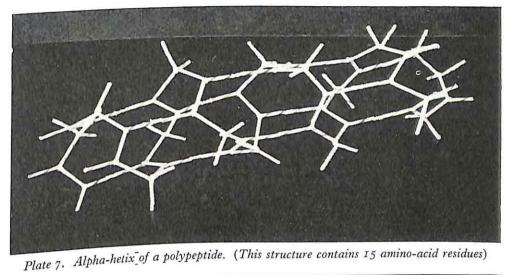


Plate 6. Two carbohydrates. L.: Sucrose. R.: Cellulose



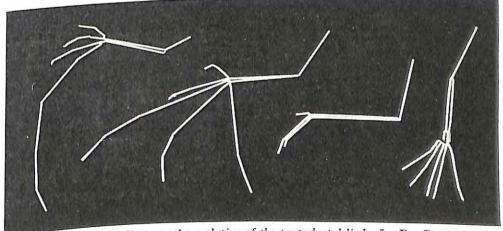


Plate 8. Models to illustrate the evolution of the pentadactyl limb. L.-R.: Pterodactyl, rat, bird, human hand

SOME USEFUL INFORMATION REQUIRED FOR BUILDING CHEMICAL STRUCTURES

1. Institute of Physics colour code

Hydrogen—White, Carbon—Black, Oxygen—Red, Sulphur—Yellow, Fluorine—Light green, Chlorine—Grass green, Bromine—Blue green, Iodine—Dark green, Phosphorus—Purple, Silicon—Grey.

2. Bond lengths (in ångströms)

C—C (paraffinic and diamond) 1·54; C—C (graphite) 1·42; C—C (olefinic) 1·34; C—C 1·20; C—C (aromatic) 1·395; C—H (paraffinic) 1·09 (this is an average value, as variation between 1·056 and 1·115 is known); C—N (3 covalent as in amines) 1·47; C—N 1·158; C—O (ethers) 1·43; C—O (aldehydes, ketones) 1·23; C—Cl 1·77; C—Br 1·94; C—I 2·13.

3. Bond angles

The technique is not sufficiently accurate for precise values of bond angles to be considered and in any case, changes in bond angle between related compounds are quite small. The following are given as a guide: H—C—H 109°; H—O—H 105°; NH₃ (pyramidal) 108°; NH₂-(planar) 120°.

References

- Dreiding Molecular Models are obtainable from Koch-Light Laboratories Ltd., Colnbrook, Buckinghamshire.
- 2. Feiser, 'Plastic Dreiding Models', J. Chem. Ed., 1963, 40, 457.
- 3. Kooyman, 'Disc-shaped Attachments for Dreiding type Molecular Models', ibid., 1963, 40, 204.
- 4. Larson, 'Atomic and Molecular Models from Vinyl-covered Wire', ibid., 1964, 41, 219.
- 5. Brumlik, Barrett and Baumgarten, 'Framework Molecular Orbital Models', ibid., 1964, 41, 221.
- 6. Models on the lines described by the authors of [5] are now obtainable from Prentice-Hall Inc., Pegasus House, Golden Lane, London, E.C.I.

2. Energetics and kinetics

2. Énergétique et cinétique

An article by Sir R. S. Nyholm and H. F. Halliwell, reproduced in the first volume of New Trends stresses the importance of energy as a unifying concept in the teaching of science. They point out that this is a way of integrating various branches of science, e.g., chemistry and physics, and also of integrating Various branches of a particular science, thus expanding the horizons of the student in science as a whole. Furthermore, considerations of energy changes are important in linking science with everyday life. These ideas are now widely accepted, and a survey of recent revisions of chemistry courses shows that the study of energy changes has been introduced at quite an early stage. The extensive use of thermometers and simple calorimeters is an excellent feature of many elementary practical chemistry courses.

It must be said, however, that there are those who feel strongly that the treatment of topics such as free energy and entropy changes in the more advanced school courses suffers from a lack of rigour. They would prefer to keep these topics for college chemistry courses, and go no further than discussions sions of equilibrium constants and relationships of the type d ln $K_p/dT = \Delta H/RT^2$ in school chemistry. Certainly it is not difficult. difficult to find examples of attempts to explain why some substances are stable and others are not, why some reactions go readily and others apparently not at all, which do not bear rigorous analysis. However, this is not a reason for not attempting to discuss and correlate energy changes in chemical reactions at a level appropriate to the age and experience of the alarmore the alar the class. The teacher must tell the truth—but not necessarily the whole truth.

BOND ENERGIES

This is a topic in which imprecise statements abound in element elementary treatments. Teachers may therefore find it helpful to work at to work through the article by S. W. Benson reproduced here. This is This is set at the college chemistry level, but a number of examUn article de sir R. S. Nyholm et H. F. Halliwell reproduit dans le premier volume des Tendances nouvelles souligne l'importance de la notion d'énergie comme facteur d'unification de l'enseignement des sciences. Les auteurs montrent qu'elle permet d'intégrer différentes branches de la science, par exemple la chimie et la physique ou bien différentes disciplines à l'intérieur d'une branche déterminée, ouvrant ainsi à l'étudiant des perspectives plus larges sur l'ensemble du domaine scientifique. D'autre part, l'étude des transformations de l'énergie est importante pour l'application de la science à la vie quotidienne. Ce sont là des idées répandues de nos jours, et une enquête sur les dernières éditions révisées des cours de chimie montre que cette étude est abordée dans les tout premiers chapitres. Beaucoup de cours pratiques de chimie élémentaire font largement appel aux thermomètres et aux calorimètres simples, ce dont il convient de se féliciter.

Force est de dire, néanmoins, que certains spécialistes reprochent un manque de rigueur à l'enseignement donné dans les classes supérieures sur des sujets tels que l'énergie libre ou les variations d'entropie. Ils préféreraient les réserver aux cours universitaires, et ne pas dépasser dans l'enseignement scolaire l'étude des constantes d'équilibre et des relations du type $d_{1n}K_p/dT = \triangle H/RT^2$. Il ne serait pas difficile de citer des auteurs qui se sont efforcés d'expliquer pourquoi certaines substances sont stables et d'autres non, pourquoi certaines réactions se déclenchent aisément tandis que d'autres s'obtiennent avec le plus grand mal, et dont les tentatives ne résistent pas à une analyse rigoureuse. Cependant, ce n'est pas là une raison pour ne pas essayer d'étudier systématiquement les transformations de l'énergie dans les relations chimiques à un niveau approprié à l'âge et à l'expérience de la classe. Le professeur doit dire la vérité - mais pas nécessairement toute la vérité.

ÉNERGIES DE LIAISON

C'est là un sujet sur lequel les manuels élémentaires abondent en imprécisions. C'est pourquoi les professeurs seront sans doute intéressés par l'article de S. W. Benson reproduit ici. Il se situe au niveau des cours universitaires de chimie, mais ples will be found which are very relevant to school courses. Some particularly valuable features of this article are the annotated bibliography and data course material, and the compilations of $\Delta\,H_{\rm f}{}^{\rm o}$ and ionization potential values for many atomic, radical and molecular species. Attention might also be drawn at this point to some other useful sets of data designed for school use: Chemical Data Book (2nd ed.), 1966, edited by G. H. Aylward and T. J. V. Findlay, published by John Wiley and the Nuffield Chemistry Data Book, 1968, published by Longmans.

CHEMICAL EQUILIBRIA

Whatever disagreements there may be about discussion of free energy and entropy in school courses there can be none so far as the importance of studying chemical equilibria is concerned. Gaseous equilibria are generally too difficult to study quantitatively in school experiments. However the techniques of manipulating gases have been greatly simplified in recent years. The introduction of glass and plastic syringes simplified the measurement of volume changes in chemical reactions (a neat experiment using gas syringes in which the volume composition of ammonia is determined is described in Nuffield Chemistry: The Basic Course, 1966, London, Longmans, p. 394. The article by T. Nishikawa shows how very simple equipment (the essential component being a flexible polythene "mayonnaise bottle") can be used to obtain useful information about a gaseous equilibrium. The volume changes are not very large but they are sufficient to illustrate the main principles.

CHEMICAL KINETICS

Two of the important questions concerning chemical reactions can be summarized as "How far?" and "How fast?". Many experiments on chemical kinetics require expensive apparatus not available to schools. The article by A. E. Trotman-Dickenson describes a kinetic experiment that only requires a balance and from which a rate equation can readily be determined.

Many students find great difficulty in accepting the statement that for a unimolecular reaction the rate is proportional to the concentration whereas in bimolecular reactions the rate is proportional to the square of the concentration. These laws and those for reactions of higher order are usually presented as summaries of experiment but, for elementary reactions, it is more satisfying to present the student with a simple interpretation in terms of collision theory—and this is done in the paper by J. Weninger.

It should be emphasized, however, that discussion of the "law of mass action" in terms of rates of reaction is not a satisfactory procedure. There are very few reactions of the type

$aA + bB \rightarrow products$

for which the rate $= k[A]^a[B]^b$. If the reaction could be broken down into its constituent steps this rate law would be valid for each separate step, but the over-all rate is not necessarily linked with the stoichiometry.

on y trouvera un certain nombre d'exemples pouvant être utilisés avec profit pour l'enseignement scolaire. Il se recommande en particulier par une bibliographie et des références annotées, ainsi que par une liste des valeurs de $\Delta H_{\rm f}^{\,0}$ et du potentiel d'ionisation de nombreux atomes radicaux et molécules. Signalons ici d'autres formulaires utiles conçus à l'intention des écoles: le Chemical data book (2° éd.), 1966, publié par John Wiley sous la direction de G. H. Aylward et T. J. V. Findlay, et le Nuffield chemistry data book, 1968, publié par Longmans.

ÉQUILIBRES CHIMIQUES

S'il peut y avoir désaccord sur l'opportunité d'étudier l'énergie libre et l'entropie dans les établissements secondaires, chacun reconnaît l'importance de l'étude des équilibres chimiques. Les équilibres gazeux sont généralement trop difficiles à étudier quantitativement au cours des travaux pratiques scolaires. Toutefois, les techniques de manipulation des gaz ont été considérablement simplifiées dans les dernières années. L'introduction de seringues en verre et en plastique a simplifié la mesure des variations de volume dans les réactions chimiques (on trouvera dans Nuffield chemistry. The basic course, p. 394, Longmans, 1966, la description d'une expérience très bien conçue, utilisant des seringues à gaz qui permettent de déterminer la composition volumique de l'ammoniae). L'article de T. Nishikawa explique comment un matériel très simple (composé essentiellement d'une « bouteille à mayonnaise » en polythène souple) peut être utilisé pour obtenir des renseignements utiles sur un équilibre gazeux. Les variations de volume ne sont pas très importantes, mais elles sont suffisantes pour illustrer les principes essentiels.

CINÉTIQUE CHIMIQUE

Deux des questions importantes qui se posent au sujet des réactions chimiques peuvent se résumer ainsi: « Jusqu'où? » et « A quelle vitesse? » De nombreuses expériences de cinétique chimique exigent un matériel onéreux, dont ne disposent pas les écoles. L'article de A. E. Trotman-Dickenson décrit une expérience de cinétique qui ne nécessite qu'une balance et qui permet aisément de déterminer l'équation de la vitesse de réaction.

De nombreux étudiants éprouvent de grandes difficultés à admettre que, dans une réaction unimoléculaire, la vitesse est proportionnelle à la concentration alors que, dans les réactions bimoléculaires, la vitesse est proportionnelle au carré de la concentration. Ces lois et celles qui concernent des réactions d'ordres plus élevés sont généralement présentées comme des conclusions d'expériences mais, pour les réactions élémentaires, il est plus satisfaisant de les présenter à l'étudiant accompagnées d'une interprétation simple fondée sur la théorie des chocs comme le fait l'article de J. Weninger.

Il faut souligner toutefois que l'application de la « loi d'action de masse » à l'ensemble de la réaction n'est pas une méthode satisfaisante. Il y a très peu de réactions du type aA+bB → produits, pour lesquelles la vitesse soit égale à k[A]^a [B]^b. Si la réaction pouvait être décomposée en ses étapes successives, cette loi serait valable pour chacune des étapes mais la vitesse globale n'est pas nécessairement liée à la stœchiométrie.



Resource Papers—III

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Bond Energies

Defore launching into our discussion of bond energies let us consider the importance of this concept to the field of chemistry and to current chemical education. If one were to divide modern chemistry up into general fields of inquiry, very high on the list in terms of importance would be the relation between molecular structure and chemical reactivity. Many chemists in fact are of the opinion that any general and detailed solution to this problem of structure and reactivity would effectively convert chemistry from a basic into an applied science.

Most chemical reactions involve the breaking of old bonds and the making of new ones. No quantitative discussion of the relation of structure to reactivity can proceed very far therefore without giving reasonably precise values for the energies and entropies involved in these processes of bond-breaking and bond-making. Reaction rates are very sensitive functions of these energies and entropies.

Let us consider an actual example. If an equimolar mixture of C2H6 and C3H8 is mixed with Br2 and exposed to blue light, a very rapid reaction can occur at about 60°C leading to metathesis reactions whose products are C₂H₅Br + HBr and *i*-propyl bromide + HBr. The yield of i-propyl bromide is over 100-fold greater than that of ethyl bromide (1). A sufficient though

not complete explanation is afforded by the knowledge that the mechanism in both instances proceeds through a radical chain (radical centers are labeled with dots):

$$B\dot{r} + C_2H_4 \stackrel{1}{\rightleftharpoons} HBr + CH_2\dot{C}H_2$$
(I)

CH₃CH₂ + Br₂ → CH₃CH₂Br + Br

$$B\dot{r} + C_3H_8 \stackrel{1'}{\rightleftharpoons} HBr + CH_3\dot{C}HCH_3$$
(II)

Steps 3 and 3' of both chains are fast, exothermic, and irreversible. Steps 1 and 1' are both slow, endothermic, and mildly reversible. At high [Br2]/[HBr] ratios the relative yields are determined only by the rates of 1 and 1'. From the relevant bond energies we can show that step 1 is 3.5 kcal more endothermic than step 1'. The activation energies for both must be in excess of the endothermicities and can be also expected to differ by about 3.5 kcal. At 60°C this will amount to a factor of $e^{-3.5/RT} = 10^{-2.3} = 1/200$ in the ratio of rate constants, k_1/k_1' . This factor becomes 1/600 at 0°C.

This example illustrates how very small differences in bond energies can lead to enormous differences in reaction rates for otherwise very similar systems. We may then agree that an understanding of bond energies is important to an understanding of the rates of chemical reactions, at least those involving atoms and radicals

However, the bulk of inorganic and organic reactions1 in solution can best be described in terms of ionic species or ion-pairs. The production of these charged species from neutral molecules also involves the breaking of bonds. In such cases we talk of these bond breaking reactions as "heterolytic" fissions. Bond breaking of molecules to produce neutral species is called "homolytic" fission. The energies of heterolytic bonds are of great importance for understanding solution reactions but we shall say relatively little about them here. The entropies of bond fission are also of great importance, but these are also outside the scope of the present discussion.

What Are Bond Dissociation Energies?

In the present article we shall define Standard Bond

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¹ For an elementary discussion of undergraduate topics in kinetics, see Benson (2).

Dissociation Energies (DH°) to mean the enthalpy change in the chemical process in which 1 mole of a specified bond is broken, reactants and products being in their standard states of hypothetical ideal gas at 1 atmosphere pressure and 25°C. Thus if A—B represents a molecule with a bond between fragments A and B, then $DH^{\circ}(A-B) = \Delta H_{r}^{\circ}$ for the process:

$$A-B(g) \rightleftharpoons \dot{A}(g) + \dot{B}(g)$$
 (III)

Since ΔH ,° is positive for an endothermic process, DH° will in general be positive also. However as will be noted later, interesting exceptions exist.

Heats of reaction may be related to heats of formation and for reaction III above:

tion and for reaction
$$H^{r}$$
 disconnection $AH_{f}^{\circ}(\dot{\mathbf{A}}) + \Delta H_{f}^{\circ}(\dot{\mathbf{B}}) - \Delta H_{f}^{\circ}(\mathbf{A}\mathbf{B})$ (1)

$$\Delta H_{r}^{\circ} = DH^{\circ}(\mathbf{A} - \mathbf{B}) = \Delta H_{f}^{\circ}(\dot{\mathbf{A}}) + \Delta H_{f}^{\circ}(\dot{\mathbf{B}}) - \Delta H_{f}^{\circ}(\mathbf{A}\mathbf{B})$$

Equations like this are very useful in relating bond dissociation energies to heats of formation and vice versa. Thus one of the earliest precise measurements of the bond dissociation energy of H_2 was by the calorimetric measurement of the heat liberated when H atoms recombined in a platinum chamber (3). This yielded for the reverse process of dissociation:

$$H_2(g) = 2\dot{H}(g)$$
 (IV)

a value of $\Delta H_r = 105$ kcal, then from equation (1) $\Delta H_f^{\circ}(H(g)) = +52.5$ kcal, a value very close to the best value of +52.1 kcal accepted today.² (See Table A-1.)

There is not much accurate data available on bond dissociation energies; however we can sometimes make use of a more readily available quantity, the "Average Bond Dissociation Energy." Thus in CH₄ there are 4 C—H bonds and for this compound we can define the Average Bond Dissociation Energy, $DH^a(C-H)$ as Average Bond Dissociation Energy, $DH^a(C-H)$ as 1 /4 of the total enthalpy required to break all of the C—H bonds in CH₄. This corresponds to the chemical process of atomization:

$$CH_4(g) \rightarrow C(g) + 4H(g)$$
 (V)

$$CH_{4}(g) \rightarrow C(g)$$

$$DH^{6}(C-H) = \frac{1}{4}\frac{\Delta H_{f}}{\Delta H_{f}} = \frac{1}{4}\frac{\Delta H_{f}}{\Delta H_{f}} (C(g)) - \Delta H_{f} (CH_{4}(g))$$
(2)

Since the relevant ΔH_f° are available for the elements, DH^{a} are easily calculated from the ΔH_f° of a given molecule. From the point of view of reactivity, however, these average BDE (bond dissociation energies) are not very interesting and can be quite misleading. Thus for the H_2O molecule we can find that DH^{a} . Thus for the H_2O molecule we can find that DH^{a} . Thus for the H_2O molecule we can find that DH^{a} . Of the first bond $DH^{\circ}(HO-H)$ and the second bond of the first bond $DH^{\circ}(HO-H)$ and the second bond $DH^{\circ}(H-O)$, namely, 118 and 103 kcal respectively. The differences are quite appreciable and very important. They can be related to the observation that OH tant. They can be related to the observation that OH radicals are much more reactive than O atoms in abstracting H atoms from stable molecules.

stracting H atoms from stable molecules. Table 6) in The differences are even greater (see Table 6) in the case of CH₄, where the first C—H bond, DH°-(CH₃—H), is 104 kcal; the second, DH°(CH₂—H), is 106 kcal; and the 106 kcal; the third, DH°(CH—H), is 106 kcal;

last, $DH^{\circ}(C—H)$, is 81 kcal. Some extreme examples are provided by CO_2 , for which $DH^{\circ}(OC—O) = 127$ and $DH^{\circ}(C—O) = 257$ kcal, and NO_3 , for which $DH^{\circ}(O_2N-O) = 50$, $DH^{\circ}(ON—O) = 72$, and $DH^{\circ}(N—O) = 151$ kcal.

At this point we must be careful to mention an implicit assumption in this discussion. To be able to talk about bond dissociation energies requires a rather complete knowledge of the structure of the molecule involved and the products to which it gives rise. Thus in the case of NO₃ mentioned above, it is assumed that it has a pyramidal or flat structure with the N atom in the center bonded to three O atoms:

However there is another form of NO₃ with the approximate structure:

and it is important to know which one is being discussed. If the structure were cyclic, as, for example

we should have great difficulty talking about a "Bond Dissociation Energy." Thus in the case of the splitting out of an O atom from ethylene oxide

$$\begin{array}{cccc}
O \\
CH_2 & CH_2 \rightarrow C_2H_4 + O
\end{array} (VI)$$

it is misleading at best to talk about a "BDE." There is no simple characterization of this reaction in terms of a BDE. In similar fashion the splitting out of a C atom from benzene has no simple description in terms of BDE, while the splitting out of an H atom from benzene has a simple meaning only if we know that the product is a phenyl radical.

$$C_6H_6 \rightarrow C_6H_5 + H$$
 (VII)

This warning is of great importance in discussing bond dissociations from ions or complex molecules where internal rearrangements are involved. Thus the ethyl carbonium ion, $C_2H_5^+$, in the gas phase may very well have the bridged structure:

If it does, the process of losing a proton

$$C_2H_5^+ \rightarrow C_2H_4 + H^+$$
 (IX)

cannot be discussed simply in terms of BDE.

Processes such as those represented by eqn. IX or its inverse are of considerable importance in organic and inorganic chemistry, and the property of "proton affinity" is perhaps a better characterization of such reactions than simple *BDE*.

The same is true of ionization processes involving electrons; they are undoubtedly better discussed in

² The best source of such data, replete with literature references, is the JANAF tables of thermochemical data (B-7) issued by the Thermal Research Laboratory, Dow Chemical Co., Midby the Thermal Research Laboratory,

terms of "ionization potentials" or electron affinities than in very dubious language in terms of BDE.

Intermolecular Forces and Bond Dissociation Energies

Bond dissociation energies readily lend themselves to simple molecular interpretation. They measure in a quantitative way the forces holding together the parts of a molecule. Our present knowledge of such forces is extremely crude and can be summarized in the diagram shown in Figure 1. There the potential energy of interaction of the neutral species A—B (which is held together by a chemical bond between A and B) is plotted as a function of the bond distance r_{AB} . The minimum in the curve occurs at the distance r_0 which would correspond to the equilibrium separations of the A and B centers in the stable molecule. The potential energy of A and B at this point is $-V_0$, measured with respect to zero potential energy at infinite separation.

The actual work required to "completely" separate A and B from each other is usually slightly less than V_0 by an amount which is due to the fact that in the A-B molecule, A and B are not at rest relative to each other but possess kinetic energy. In Figure 1 this kinetic energy is equal to $(V_0 - D_0)$ so that the work of separation of A and B is equal to D_0 . This residual kinetic energy associated with chemical bonds is called the zero point energy. For simple diatomic molecules it is equal to $1/2h\nu_0$ where ν_0 is the vibration frequency and h is Planck's constant. For H2 with a high frequency $(\nu_0 = 4400 \text{ cm}^{-1})$ it amounts to 6.4 kcal/mole, while for $D_2(\nu_0 = 3120 \text{ cm}^{-1})$ it is 4.5 kcal/mole. This difference in values accounts for the fact that D2 is more difficult to dissociate than H2 by 1.9 kcal/mole (Table 1). For molecules with much lower frequencies such as I_2 ($\nu_0 = 215$ cm⁻¹) the zero point energy is only 0.3 kcal/mole.

In general DH° (A—B) differs from both D_0 and V_0 . The quantity $D_0(A$ —B) corresponds to the bond dissociation energy at 0° K, all species considered to be ideal gases. The two quantities differ by the net enthalpy change in raising the system from 0° K to the standard temperature of 25°C. If A—B is a simple diatomic molecule with a high frequency, and A and B are simple atoms, they have energy contents at 298°K relative to 0° K of ${}^{5}/{}_{2}RT$, ${}^{3}/{}_{2}RT$, and ${}^{3}/{}_{2}RT$ respectively assuming that A and B have only 1 ground electronic

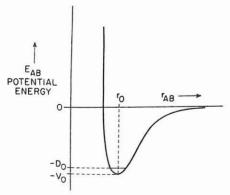


Figure 1. Simple schematic, potential energy diagram for the molecular species A—B showing the potential energy of the A—B bond as a function of the bond length, r_{AB}. A and B may be atoms and/or radicals.

Table 1. Bond Dissociation Energies (kcal/mole) of Some Diatomic Inorganic Molecules and Radicals

Species	DH°	Species	DH°	Species	DH°
H_2	104.2	Н—О	102.4	Be-F	147
D_2	106.0	HF	135.8	MgF	107
O_2	119.2	H-Cl	103.0	Al—F	159
N_2	226	H—Br	87.5	C-F	116
P_2	117	H-I	71.3	Na-F	115
Sb_2	70	H-C	81	Cl—F	61
C_2	143	H-N	86	Br-F	60
Si_2	81 ± 9	H-S	85	IF	58
Pb_2	13 ± 5	HNa	48	I—Cl	50
S_2	101	H-Hg	7	Br-Cl	52
\mathbf{F}_2	38	N-O	151.0	B-Cl	119
Cl_2	58	C-O	256.9	Al-Cl	118
Br_2	46.0	Si-O	190 ± 4	Hg-Cl	24
I_2	36.1	s-0	125	Ag—Cl	75
Na_2	18.7	В—О	187 ± 12	Cu-Cl	78
K_2	12.2	P—O	141	Na-Cl	98
Cu_2	46 ± 3	Cl—O	64	Be-Cl	104
Ag_2	38 ± 3	Al—O	117		-01
		Be-O	107		
		Mg-O	91		

state. Being ideal gases their enthalpy contents are just RT greater:

$$H = E + PV = E + RT \tag{3}$$

Thus in this simple case $DH^{\circ}(A-B)$ is just $^3/_2RT \approx 0.9$ kcal greater than $D_0(A-B)$. This is lowered if the A-B frequency is much lower. Although these differences are small; i.e.—of the order of 1 kcal—they have been the cause of considerable confusion in that some authors have employed BDE to refer to the energy change (ΔE) rather than the enthalpy change (ΔH) in the dissociation process at 25°C. These differ by precisely RT (eqn. 3) or 0.6 kcal. Still other authors have used D_0 at 0°K as BDE.

For more complex molecules such as ethane (C2H6), the process of breaking the central C-C bond is accompanied by many other structural changes in the residual CH3 fragments. These include changes in the C—H distances and H—C—H angles and hence also in the fundamental frequencies and so in the net zero point energies. Ethane has 3 translational degrees of freedom, 3 rotational degrees of freedom and 3n-6 =18 internal vibrations, one of which is a hindered rotation. Methyl radicals on the other hand have each 3 translations, 3 rotations, and 6 internal vibrations. At room temperature, C2H6 and CH3 each have enthalpies of $^8/_2RT = 2.4$ kcal due to rotation, translation and PV. Thus $DH^{\circ}(CH_3-CH_3)$ is 2.4 kcal greater than D_0 . However, E₀°(C₂H₆), the zero point internal energy of C2H6, is 45.0 kcal4 while that of each CH3 is 18.2 kcal

³ It is to avoid this confusion that we have adopted the nomenclature DH° to describe BDE. The H symbol emphasizes, in accordance with thermodynamic usage, the enthalpy character of our BDE. We have chosen to adopt 25°C as our standard temperature to follow the international thermodynamic convention.

The zero point energies are estimated from the relation $E_0^\circ = h/2\sum \nu_t$ where ν_t are the internal normal modes of the species. For polyatomic molecules we have used Herzberg, G., "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules," D. van Nostrand Co., Inc., New York, 1951. For CH₃ we have used the JANAF (B-7) assignments. An alternative method of assigning average frequencies leads to values identical to within about 6%. For this, the average frequencies given by Meghreblian, R. V., J. Am. Rocket Soc., 128 (1951), work very well. See also (B-8).

so that in this case $V_0 = D_0 + 45.0 - 2 \times 18.2 = D_0 + 8.6$ kcal, a substantial correction. However $DH^{\circ} = V_0 + 6.2$ kcal, a lesser change.

These relations are shown plotted in Figure 2. The minimum in the curve at $-V_0 = -94.2 \pm 1$ kcal represents the true potential energy of the CH3-CH3 interaction in C_2H_6 . D_0 is equal to $V_0 - E_0^{\circ} = 94.2$ -45.0 = 49.2 kcal.

At the right hand side of Figure 2, 2E0°(CH3) represents the total zero point energy of two CH3 radicals while H_{τ}° represents the increase in enthalpy in going from 0°K to 25°C. We see that DH°(CH₃-CH₃), indicated by the length of the arrow in the diagram is a complex quantity not simply related to V_0 . If we are going to discuss BDE in terms of molecular interactions we should really use V_0 , not DH° . In general they will differ by about 6 kcal for hydrocarbons and by lesser amounts for systems with heavier atoms and lower frequencies. Fluorocarbons will show differences of the order of only 2 kcal.

Methods of Measuring Bond Dissociation Energies

Since our definition of BDE corresponds to the heat of a specified reaction (eqn. 1), it is a thermochemical quantity which can be measured by any of the techniques available for the measurements of heats of reac-These can be generally divided into two groups, measurements and non-equilibrium measurements. Ideally, equilibrium measurements are the only precise method for measurement of thermochemical quantities. The accuracy of any non-equilibrium measurement depends on the extent to which the lack of equilibrium has perturbed the properties we are measuring. This is not always known or ascertainable and accounts for much of the controversy in the literature on BDE. Since many of the details of these measurements are covered in our references we shall consider the methods only very briefly.

Equilibrium Measurements

If we can measure the equilibrium composition of a system containing A-B, A, and B at some specified temperature, then we can obtain the equilibrium constant K and also the free energy change for the dissociation:

the free energy
$$A - B \implies A + B$$

$$K = \frac{[A][B]}{[A - B]}$$

$$\Delta G^{\circ} = -RT \ln K = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\Delta G^{\circ} = -RT \ln K = \Delta H^{\circ} - T\Delta S^{\circ}$$
(5)

$$AG^{\circ} = -RT \ln K = \Delta H^{\circ} - T\Delta S^{\circ}$$
(5)

To obtain ΔH° we must either know ΔS° from independent sources or else measure ΔG° at two sufficiently different temperatures so that average values for ΔS° and ΔH° in the temperature interval can both be obtained. Since ΔC_p for most reactions not involving changes in numbers of moles of charged particles in a solvent are small, the variations in ΔH° and ΔS° over a temperature range of even 200°C will also be small.

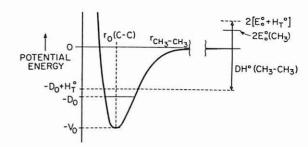


Figure 2. Schematic potential energy diagram for the dissociation of $r_{\rm CH_6}$ into 2 CH₃ radicals. Potential energy of the C—C bond is plotted as ordinate against $r_{\rm C}$ —C, the C—C bond length as abscissa. The minimum in the curve, $r_{\rm O}$, corresponds to the equilibrium C—C distance of . 1.54 A.

Thus the average values for ΔH° and ΔS° will differ little from the correct values anywhere in such a temperature range. This procedure is of course equivalent to the van't Hoff relation for equilibrium constants:

$$\Delta H^{\circ} = \frac{RT_1T_2}{T_1 - T_2} \ln \left(K_1/K_2 \right) \tag{6}$$

The thermodynamic method has the virtue that even poor measurements of K can give ΔG° to good accuracy. Thus at T = 500°K, an uncertainty in K of $\pm 10\%$ will lead to an uncertainty in ΔG° (from eqn. 5) of only ±0.1 kcal. However this is magnified by roughly the ratio of $T_1/(T_1-T_2)$ in determining ΔH° from the van't Hoff relation (eqn. 6). If $T_1 - T_2$ is 50°K centered about 500°K, then the 10% uncertainty in K_1 and K_2 each contribute ± 1 kcal to ΔH° for a total uncertainty given by their vector sum, ± 1.4 kcal.

The other virtue of the thermodynamic method is that the reactants need not be pure; catalysts or impurities can only help the attainment of equilibrium, and irreversible side reactions are important only if they are rapid relative to the rate of attainment of equilibrium.

An alternative to the use of the van't Hoff relation is to measure or estimate ΔS° independently. In a large number of cases this can be done by either statistical methods or empirical rules to an uncertainty of usually less than ±1 cal/mole-oK. This would introduce an uncertainty into ΔH° (eqn. 5) of ± 0.5 kcal/mole at 500°K. An uncertainty in ΔS° of ±2 cal/mole-°K would only contribute ± 1.0 kcal to ΔH° at 500°K. Unless K can be determined to better than $\pm 10\%$ this method of estimating ΔS° is decidedly superior to the use of the van't Hoff relation for determining ΔH° .

Equilibrium methods have been employed in this fashion to measure $DH^{\circ}(O_2N-NO_2)$; $DH^{\circ}(I-I)$, $DH^{\circ}(C-C)$, $DH^{\circ}(O-H)$ and $DH^{\circ}(F_2N-NF_2)$. For ideal gases at temperatures where dissociation is appreciable, the composition and thus K are obtained merely from P-V-T measurements at known gas den-This was the case for the classical measurements on $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium⁶ and also for $I_2 \rightleftharpoons 2I$ (5). Where dissociation is very small but the species can be observed spectroscopically because of their very large absorption coefficients, spectrophotometric methods can

⁵ For gas reactions involving a change in the number of moles, ΔC_p are in the range of 1-6 cal/mol $^\circ$ K. For solution reactions involving ions, such as the ionization of a weak acid, ΔC_p can be involving ions, such as the ionization of a weak acid, ΔC_p can be of the order of -21 to -30 cal/mole °K and both ΔH and ΔS will change markedly with temperature.

⁶ See Giauque and Kemp (4) for a discussion of the measurements.

be used to determine the composition. This has been done with OH in the system $^{1}/_{2}O_{2} + H_{2}O \rightleftharpoons 20H$ to obtain $\Delta H_{f}^{\circ}(OH)$ (6) and for $N_{2}F_{4} \rightleftharpoons 2NF_{2}$ (7). In each such case however some independent calibration is necessary so that the absolute value of the absorption coefficient of the species being observed—either OH (6) or NF₂ (7) radical—can be measured. This is not always a simple matter and can be ridden with errors.

It is clear that the methods of analysis of equilibrium systems are limited only by the ingenuity and financial means of the investigator, so that there is not much point to cataloging here the arsenal of analytical techniques available. They include measurements of such properties as magnetic susceptibility, nuclear magnetic spin resonance, electron spin resonance, molar volume (e.g., dilatometry), molar refraction (usually by interferometer), speed of sound, and mass spectroscopic analysis. All require careful calibration and special precautions but can be used to good advantage.

Spectroscopic Methods

For diatomic molecules, it is frequently possible to make a sufficiently detailed analysis of the electronic absorption or emission spectra so that all of the vibrational energy levels of the potential energy curve can be observed and extrapolated to the limit of zero potential energy (see Fig. 1).8 If in addition the electronic states of the atoms are known, then such analysis yields the value of D_0 (Fig. 1) directly. Such analyses have been performed for H_2 , O_2 , I_2 , Br_2 , and Cl_2 among others. For N_2 , S_2 , NO, and CO, these methods were not sufficient to give unique values. However once an independent method made it possible to select one of the choices as most probable, the spectroscopic method could yield the most precise value of the BDE.

Mass Spectrometric Methods

One of the very popular methods for measuring BDE has been by use of a mass spectrometer to measure the threshold electron energies required to produce a known set of fragments from a given molecule. These threshold energies are known as Appearance Potentials (AP) and are usually given in units of electron volts (1 ev = 23.05 kcal/mole). Thus for H_2 molecules, it is found that they yield H^+ ions in the mass spectrometer at an electron energy of $18.0 \pm 0.1 \text{ ev}$. If we assume that this is the heat of the following reaction

$$18.0 \text{ ev} + \text{H}_2 \rightarrow \text{H}^+ + \text{H}^- + e^-$$
 (7)

then since the heat of formation of H^+ is known from its ionization potential (IP = 13.60 ev, Table A-9):

$$13.60 \text{ ev} + \text{H} \rightarrow \text{H}^+ + e^-$$
 (8)

we can subtract these two equations to obtain:

$$4.4 \text{ ev} + \text{H}_2 \rightarrow 2\text{H} \tag{9}$$

⁹ For detailed discussion see Franklin and Field (B-3).

This gives $4.4 \times 23.05 = 101.5 \pm 2.3$ kcal/mole for the BDE of H_2 in good agreement with the spectroscopic value of 104.2 kcal/mole. For more complex species such as CH_4 one can measure the appearance potentials to form CH_3 + from CH_4 and independently the ionization potential of CH_3 . If we can assume these correspond to the processes:

$$AP (CH_3^+) + CH_4 \rightarrow CH_3^+ + H + e^-$$
 (10)

$$IP (CH_3) + CH_3 \rightarrow CH_3^+ + e^-$$
 (11)

we see that $DH^{\circ}(CH_3-H)$ is given by the difference:

$$DH^{0}(CH_{3}-H) = AP(CH_{3}^{+}) - IP(CH_{3})$$
 (12)

While in many cases the values of BDE obtained mass spectrometrically are in good agreement with independently measured or more reliable values, they are also frequently in gross disagreement. As a result they have not been a very useful method for obtaining BDE with an accuracy of better than ± 6 kcal.

The reasons for this low precision lie principally in the fact that in ionization processes by excited electrons (eqns. 10 and 11), the thermodynamic state of the final products is not well known. If for example the CH_3 + ion from CH_4 is produced with excess energy of any kind—translational, vibrational, or electronic—then the measured $AP(CH_3+)$ is too high. Simple ionization potentials (eqn. 11) are likely to be reasonably accurate where the initial state of the species is well defined and there are no large structural changes on ionization. Where structural changes do occur, the values of IP have considerable error. A good example of this is provided by the case of NO_2 for which at present no reliable IP is known either from optical spectroscopic or mass spectrometric measurements.

In the ground state, NO₂ is a non-linear symmetrical molecule. The NO distance is 1.19 Å and the central angle is 134°. The NO₂+ ion is linear in its ground state with a shorter NO distance (1.15 Å). In order for NO₂ to assume the NO₂+ structure on ionization by a photon (optical) or electron collision, the N atom must move 0.47 Å relative to the two O atoms. However at comparable energies the electron in NO₂ is moving about 150 times faster than the N atom. If we assume that the ionization process is completed in the time it takes the electron to move 30 Å (at which point its energy of interaction with the residual positive ion is less than 11 kcal), the N atom has moved less then 0.2 Å¹⁰ and is not even close to its equilibrium position in NO₂+.

It should finally be commented that in a dissociation process such as given by equations (7) and (10) the fragments may come off with less than thermal translational or rotational energies. In such cases the appearance potentials can actually be too low by amounts of the order of from RT to 5/2 RT, which at $T=300^{\circ} K$ can represent an error of from 0.6 to 1.5 kcal/mole.

Kinetic Methods

The large majority of our currently available BDE for molecules more complex than triatomics have been

⁷ For molecules, the absorption coefficients can be sensitive to both temperature and pressure. For diatomic molecules where the spectra consist of very narrow lines, an excellent spectrometer of high resolving power is needed to measure true optical absorption.

⁸ The extrapolation method is referred to as a Birge-Sponer extrapolation and is described in many texts and references. See for example Gaydon (*B*-4).

¹⁰ Note that the electron still has energy in excess of escape energy at this point by more than 11 kcal or 0.5 ev. Its average energy during the ionization process must have been about 5 ev corresponding to a much higher average velocity.

Table 2. Bond Dissociation Energies (kcal/mole) for Some Organic Molecules R'-R"

$\Delta H_f^{\circ} \rightarrow$	(52.1) H	(18.9) F	(28.9) Cl	(26.7) Br	(25.5) I	(9.3) OH	(40 ± 2) NH ₂	$\mathop{\rm OCH_1}^{(2\pm1)}$	(34 ± 1) CH ₁	(26 ± 1) C ₂ H ₅	(17.5 ± 1) i-C ₂ H ₇	(6.7 ± 1) t-Bu	(71 ± 2) C ₆ H ₆
34 ± 1) CH ₁ 26 ± 1) CH ₁ 21 ± 1) r-C ₁ H ₁ 21 ± 1) r-C ₂ H ₁ 17.5 ± 1) t-C ₃ H ₁ 6.7 ± 1) t-Bu 71 ± 2) C ₄ H ₁ 45 ± 1) C ₄ H ₂ CH ₂ 38 ± 1) allyl -4.0) CH ₂ CO -6 ± 2) CH ₂ CH ₂ O -6 ± 2) CH ₂ CH ₂ O -3 ± 2) CH ₂ =CH	104 98 98 94 5 91 1103 85 85 87 5 102 90 103	108 106 106 105 116	83.5 81.5 81.5 81 78.5 83.5	70 69 69 68 63 72 	56 53.5 53.5 53 49.5 40 41 52.5	91.5 91.5 91.5 91.5 90.5 103 77 77.5 109 43 28°	79 78 78 77° 77° 91 96° 	80 80 80 80 . 5 78 91 66° 66° 44° 21° 87	88 85 85 84 80 93 72 72 82 80 72 92	85 82 82 80 77 90 69 69 79 80 72 89	84 80 80 77.5 73 87.5 67.5 67 81 81 71° 87	80 77 77 73 67.5 84 64 63 80 69 ^a 84	93 90 90 87.5 84 100 78.5 77 89 91 84 ^a 99

a Estimates by the author.

provided by kinetic studies. In general these are also more reliable than comparable values from mass spectrometric methods, the only other general source for such values.¹¹

The possibility of obtaining BDE from kinetic studies rests on two major premises: (a) that the kinetic study can yield an accurate rate constant and Arrhenius parameters for a simple molecular reaction, and (b) that the activation energy so measured can be identified with a heat of reaction. Let us consider some examples.

Di-t-Butyl Peroxide. The thermal decomposition of ditertiary butyl peroxide in the gas phase has been carefully studied by a number of different laboratories in the temperature range 90–160°C. In this range the reaction appears to be a reasonably simple free radical one, consisting of only a few steps and not involving any chains. 12 The mechanism is:

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{1} 2(CH_3)_3CO$$

$$(CH_3)_3CO \xrightarrow{2} CH_3COCH_3 + CH_3$$

$$2\dot{C}H_3 \xrightarrow{3} C_2H_6 \qquad (X)$$

$$CH_3 + CH_3COCH_3 \xrightarrow{4} CH_4 + CH_2COCH_3$$

$$\dot{C}H_3 + \dot{C}H_2COCH_3 \xrightarrow{5} CH_3CH_2COCH_3$$

with an over-all stoichiometry in this range:

(CH₃)₃COOC(CH₃)₃
$$\xrightarrow{\sim 90\%}$$
 2CH₃COCH₃ + C₂H₆
(CH₃)₃COOC(CH₃)₃ $\xrightarrow{\sim 10\%}$ CH₃COCH₃ + C₂H₃COCH₃ + CH₄
(XI)

The observed first order rate of decomposition for such a scheme then yields the rate constant k_1 and from the temperature dependence of k_1 , its Arrhenius parameters E_1* and A_1 are obtained. Now it is common experience that radical recombinations proceed without activation energies, so it may be assumed that the observed activation energy E_1* is the same as the ΔH of reaction 1 of eqn. (X). Thus $\Delta H_1 = \Delta E_1 + RT = DH_T^{\circ}(tBuO-OtBu)$ where T is the mean temperature for the pyrolysis ($\sim 140^{\circ}\text{C}$). Correcting back to room temperature we find $DH^{\circ}(tBuO-OtBu) \simeq E_1*$ with an uncertainty of about ± 1 kcal.

Independent estimates of the *BDE* indicate that the various assumptions made are justified. *BDE* to such precisions are not attainable by any other methods, a result which has made the kinetic method extremely attractive.

Bromine + Methane. One of the first such studies which yielded the first reliable result on the C—H bond strength in CH_4 was a kinetic study of the reaction of $Br_2 + CH_4$ (9).

The thermal reaction follows the two-center chain scheme:

$$M + Br_2 \rightleftharpoons M + 2 B\dot{r} (K_{eq})$$

 $\dot{B}r + CH_4 \rightleftharpoons CH_3 + HBr$
 $\dot{C}H_3 + Br_2 \rightleftharpoons CH_3Br + \dot{B}r$ (XII)

From the kinetics it is possible to obtain values for k_1 and the ratio k_2/k_3 . From studies of the temperature dependence of these quantities it is possible to obtain the activation energy E_1^* and the difference $E_2^*-E_3^*$. From independent studies (10) it was shown that $E_3^*=1\pm 1$ kcal so that an absolute value of $\Delta H_{1,2}=E_1^*-E_2^*$ was available to a precision of ± 1 kcal. Since $\Delta H_{1,2}=DH^\circ(\mathrm{CH}_3-\mathrm{H})-DH^\circ(\mathrm{H}-\mathrm{Br})$ and $DH^\circ-(\mathrm{H}-\mathrm{Br})$ were known accurately, $DH^\circ(\mathrm{CH}_3-\mathrm{H})$ could be finally obtained as 104 kcal to within this same accuracy of ± 1 kcal.

Because the activation energies of the reaction of \dot{R} with HI to form RH + I * exothermically also appears to be about 1.5 \pm 1 kcal, the attack of I atoms on hydrocarbons has been very effectively used to obtain C—H bond energies with excellent precision (11).

While the use of kinetic studies for measuring BDE seems very attractive, the method requires careful justification in each case to see that the various assumptions underlying the method are valid. This has not always been true and accounts for some of the discrepancies which have appeared in the BDE literature. The measurement of kinetics in high temperature flow systems is always less precise than studies in stationary systems; BDE values obtained from such studies invariably have errors of the order of ± 4 kcal or higher. This has not always been realized by the workers performing the measurements.

Some Representative Values of Bond Dissociation Energies

In the Appendix will be found tables listing the standard heats of formation (ΔH_f°) of a number of atoms, molecules and radicals in the ideal gas state. From

¹¹ This statement undoubtedly represents in part a bias of the author whose interests are centered in kinetics. The reader is advised that some mass spectroscopists would take issue with this advised that some mass spectroscopists and Benson (8).

point of view.

12 For a recent summary see Batt and Benson (8).

13 Thermodynamics requires that $\Delta E_1 = E_1^* - E_{-1}^*$, where E_{-1}^* is the activation energy for the reverse reaction.

these, with the aid of equation (1), it is possible to evaluate the relevant DH° . Tables 1 and 2 contain a number of such BDE of common interest. Many more values can be evaluated from the Appendix than are listed in Tables 1 and 2.

The very first questions we may ask in connection with these tables is, "Do such values fall into any regular pattern?" "Are there any broad generalizations one may make?" A quick perusal of the values for BDE of diatomic species listed in Table 1 will soon convince one that the answer to these questions is a cautious "No." One can say perhaps that main group metals form relatively weak bonds with each other in diatomic species and stronger bonds with non-metals. The evidence for this is however not too abundant. Too much information is lacking on such species as AlCs to extrapolate even such a "weak" conclusion too far. In fact what is most striking about such a table is the numerous surprises and exceptions which occur.

For example, one of the common approaches to single bonds is to look at them from the standpoint of "electronegativity." Pauling (B-12) originally suggested that in the reaction $A_2 + B_2 \rightarrow 2AB$, the heat of the reaction should exceed zero (i.e., be exothermic) as the difference in electronegativities between A and B increased. This implied that all such reactions were either thermoneutral or exothermic. While this was generally the case, it was not true for Na₂ + H₂ → 2 NaH, which is endothermic by 26.5 kcal! It is also not true for Hg2 + Cl₂ → 2 HgCl, which is endothermic by 10 kcal or more depending on the bond energy one is willing to assign to the complex, Hg2. Although the HgO molecule is not known in the gas phase, the instability of the solid allows us to put an upper limit on its BDE of about 26 kcal, which would make the reaction $Hg_2(g) + O_2(g) \rightarrow$ 2HgO(g) endothermic by more than 66 kcal. All the alkali metal hydrides are in fact exceptions.

Table 3 contains a number of such endothermic reactions. To some of these, objections may be raised on the ground that they involve changes in multiple bonds. However we shall see later that there are no truly simple situations involving "single" bonds.

Table 3. Heats of Some Endothermic Metathesis Reactions Between Diatomic Species, $A_2 + B_2 \rightarrow 2AB$ (kcal/mole)

$Na_2 + H_2$	-	2NaH - 26.5
$Hg_2 + Cl_2$		2 HgCl - (> 10)
$Hg_2 + O_2$	\rightarrow	2 HgO - (> 66)
$N_2 + O_2$	-	2NO - 43
$N_2 + P_2$	\rightarrow	2NP - 7
$H_0 + O_0$	\rightarrow	20H - 18.6
$C_2 + N_2$	-	2CN - 19
$Cl_2 + O_2$	\rightarrow	2ClO - 48

Pauling had noted that reactions between species with very different bond strengths generally deviated from the rule, and so proposed a new rule of the geometric mean: that the *BDE* of A—B deviates from the geometric mean of the *BDE* of A—A and B—B as the difference in electronegativity between A and B differs from zero. This still has difficulties associated with it, but we shall not pursue them here.

Let us consider the classic example of the hydrogen halides. In the sequence H—F, H—Cl, H—Br, H—I, the values of DH° decrease monotonically—136, 103,

88, 71 kcal respectively. This is ascribed to the decrease in electronegativity from F to I, H and I having nearly the same electronegativities. However in the regular sequence F—F, F—Cl, F—Br, F—I the values of DH° are 38, 61, 60, 58 kcal respectively. The value of $DH^{\circ}(F_2)$ is strikingly exceptional while the other DH° show very little variation with large changes in electronegativity.

If we choose polyatomic groups where no multiple bonding is involved then we find that whereas H and CH₃ groups should have about the same electronegativity the reaction $H-H+CH_3-CH_3 \rightarrow 2CH_3-H$ is exothermic by 15.6 kcal. On the other hand CH₃-CH₃ + I₂ \rightarrow 2CH₃I is endothermic by 11.9 kcal. Table 4 lists a number of such metathesis reactions chosen to emphasize the ranges of "normal" behavior.

Table 4. Heats of Some Metathesis Reactions Between Polyatomic Molecules, $A_2 + B_2 \rightarrow 2AB$ (kcal/mole)

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
10 3.9
0.0
CN +10 CN - 5 N -16
-H +15.6 -Cl +21.4 -I -11.9
-H + 3.0 -CH ₃ - 1.6 -Br - 2.0
$=CH-CH_3 - 3.7$

We have already seen in our early discussion (p. 503) that the strength of a given bond varies considerably depending on its immediate molecular environment. There the range of BDE was quite large and the interpretation of this range in such cases as DH°(C≡O) versus DH°(OC=O) was somewhat obscured by problems of multiple bonding. Table 5 gives a range of O-H, C-H, and C-C single bond strengths for different atomic environments. What is most impressive is the range of variation in each list. Single O-H bonds vary from 119 kcal in HOH to lows of about 79 in HONO and HOCl; ±20 kcal, approximately, from the mean value of 100 kcal/mole. Similarly C-H bonds in molecules vary from 74-130 kcal, almost a factor of 2 in range. We find a similar variation in the values of C—C single bonds, from a low of 15 kcal in hexaphenyl ethane to highs of 144 and 150 in cyanogen and diacetylene.

A number of reasons have been put forward to explain the extent of these ranges of BDE; two of them, steric strain and "resonance," have a good physical basis. However no good explanations have yet been offered to account for the large difference of 17 kcal between $DH^{\circ}(HO-H)$ and $DH^{\circ}(CH_3O-H)$ or the further decrease of 12 kcal in $DH^{\circ}(HO_2-H)$. Among the hydrocarbons we note a similarly dramatic range of C—H values going from 98 kcal for $DH^{\circ}(C_2H_5-H)$ to 130 kcal for $DH^{\circ}(H-CN)$ and 125 kcal for $DH^{\circ}(H-C_2H)$. A number of authors (12) have proposed that the state of hybridization of an atom influences the strength of its bonds, and this is amply

Table 5. Effects of Near Neighbor Atomic Environments on Some O—H, C—H, and C—C Single Bond Strengths in Molecules

Species RO—H	DH° (RO—H) kcal/mole	Species Containing C—H	DH° (C—H) kcal/mole	Molecules Containing C—C	DH° (C—C) kcal/mol
HO—H CH ₃ CO ₂ —H CH ₃ O—H O ₂ NO—H HO ₂ —H C ₆ H ₃ O—H ONO—H ClO—H	119 112 102 101 90 85 79 78	CH ₃ —H CH ₃ CH—H (CH ₃) ₂ CH—H (CH ₃) ₂ C—H CH ₄ CH—H CH ₂ CH—H HCC—H NC—H CLH—CH—CH——H CC ₆ H ₃ C) ₂ C—H CC ₆ C—H F ₃ C—H HOCH ₂ —H HOCH ₂ —H	104 98 94.5 91 103 103 ~125 130 85 85 75 96 104 93 90	CH ₃ —CH ₃ CH ₄ CH ₂ —CH ₃ (CH ₃) ₂ CH—CH ₃ (CH ₃) ₂ CH—CH ₃ (CH ₃) ₃ C—C(CH ₃) ₃ C ₆ H ₃ CH ₂ —CH ₃ all ₂ I) ₂ —CH ₃ CH ₃ CO—CH ₃ CH ₃ CO—CH ₃ CH ₃ CO—COCH ₄ HOCH ₂ —CH ₃ (C ₆ H ₅) ₃ C—C(C ₆ H ₅) ₃ HCC—CCH NC—CN CH ₂ —CCH CH ₃ —CCH CH ₄ —CH ₃ C ₆ H ₅ —CH ₃	88 85 84 80 67.5 72 72 82 70 83 15a 150 144 128 122 117 100 100 93 29

^o Estimate for gas phase. Measured value in solution is 11.5 kcal/mole.

demonstrated (Table 5) by the variation in C-C bond energies from 88 kcal in $\mathrm{CH_3}\mathrm{-CH_3}$ to 100 kcal in butadiene and 150 kcal in diacetylene. If this range of DH° -(C-C) is to be attributed to hybridization it far exceeds the values so far attributed to such effects (B-11).

One point must be made at this time in connection with the range of single bond energies listed in Table 5: some of the theories which have attempted to relate bond energies and bond lengths to bond orders (i.e., bond multiplicity) in a simple fashion cannot possibly make sense for these O—H and C—H bonds which cannot be other than single bonds.

The present data do not lend themselves to any simple theoretical or empirical generalization. Rather they call attention to the fact that there is now a very rich and growing body of data on bond energies which is in serious need of theoretical explanation.

Structural Aspects of Bond Dissociation Energies

If there are no broad generalizations that one can draw concerning bond strengths, there are certainly a number of limited trends which can be well correlated with structural changes. We shall consider these individually.

Bond Dissociation Energies in Radicals—Multiple Bond **Formation**

If we consider C—H bonds as examples we find (Table 1) that in the alkanes, $DH^{\circ}(RCH_2-H)$ is 98 \pm 1 kcal independent of the nature of R, i.e., branched or unbranched (R \neq H). However if R contains a free valence in the α position, then the value of DH° is lowered by about 60 kcal (Table 1). Thus $DH^{\circ}(CH_2-CH_2)$ CH₂—H) = 39 kcal/mole compared with DH°(CH₃-CH₂—H) = 98 kcal/mole. The classical explanation for such behavior has been that in the process of removing the second H atom from C2H5 we also form a double bond. In fact, we can make an operational definition of the strength of this second or pi bond,

 $H_{\tau}(C=C)$, by equating it to the difference in strengths of the first and second bond dissociation energies.

$$H_{\pi}(C=C) = DH^{\circ}(CH_3CH_2-H) - DH^{\circ}(CH_2CH_2-H)$$
 (13)

Similarly we can define other multiple bonds as:

$$H_{\tau}(H_2C=O) = DH^{\circ}(H_3CO-H) - DH^{\circ}(H_2\dot{C}O-H)$$
 (14)

$$H_{\pi}(C \equiv C) = DH^{\circ}(H_{2}CCH - H) - DH^{\circ}(HCCH - H)$$
 (15)

However in interpreting such values one must constantly bear in mind that the quantities so defined may not be independent of other molecular changes which one may make in the structure. In Table 6 are listed a number of BDE for O-H, C-H, and C-C bonds in selected radicals. From the values listed we can deduce that the pi bond in acetylene is about the same as that in ethylene, 60 kcal, while $H_{\pi}(CH_2=0)$ is 71 kcal and the second H_{π} in allene is about 43 kcal, considerably less than the value of H_{π} in propylene of 58.5 kcal. This reduction in pi bond energy for two adjacent pi bonds is however comparable to the lowering of the $H_{\tau}(C=C)$ in ketene to a value of 50 kcal.

Such multiple bond formation affords a reasonable explanation for the fact that the R-C bond in R- \dot{C} =O radicals are all about 70 ± 3 kcal weaker than the corresponding R-C bond in R2CO. This suggests that CO has a triple bond, :C:::O: and that the pi bond energy of the third bond is 70 ± 3 kcal, a point of view entirely compatible with high bond strength of 257 kcal. This incidentally is the largest known bond strength for a molecule. The same explanation now makes it reasonable that DH°(OC=O) = 127 kcal while DH°(H₂C=O) = 175 kcal, a much higher value. Breaking the former double bond is partially compensated by the formation of a pi bond.

Table 6 is noteworthy in introducing our first unstable radical, acetate, whose $DH^{\circ}(CH_3-C\dot{O}_2) =$ -20 kcall

Resonance Effects-Fractional Bonds

Although we have seen that the range of O-H,

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C—H, and C—C single bond strengths is large, it may be noted that certain of the low values can be correlated with the appearance of multiple bonds two bonds away from the bond being broken. Thus the methyl C—H bond in propylene has $DH^{\circ}(CH_2CHCH_2—H) = 85$ kcal whereas for all other paraffin hydrocarbons $DH^{\circ}(RCH_2—H)$ does not deviate from 98 kcal by more than ± 1 kcal. This 13 kcal lowering of the usual C—H bond energy is ascribed to resonance in the resulting allyl radical. The description of the state of the radical in terms of shared electrons is that it contains two 3-electron bonds as follows:

The extra electron is then distributed between the two terminal C atoms. The implication of such a description is that two 3-electron bonds are about 13 kcal stronger than the one single and one double bond that would occur in the conventional non-symmetrical structure for the allyl radical:

From purely electrostatic considerations such a result seems quite reasonable since the number of bonding electrons is the same in the two structures XIII and XIV but in XIII we have reduced the amount of electron-electron repulsion by making a more uniform distribution of electric charge. The grandparent of all such resonance behavior, benzene may be described as having six 3-electron bonds (XV) rather than three single and three double bonds (XVI).

It is very unlikely to be fortuitous that the experimentally observed resonance energy of benzene, 37 kcal, is roughly three times the allyl resonance energy of 13 kcal. Unfortunately there is no quantitative theory to account for such results.

From the observation that bonds to benzyl are weaker by about 13 to 14 kcal than normal bonds, one can obtain a resonance energy for the benzyl radical of about 13 or 14 kcal, indicating that phenyl is equivalent in its structural effects to a double bond.

Fractional bond formation appears to occur in other systems without resonance and exerts a similar lowering effect on bond energies. Thus the bonds in R—NO and R—NO₂ compounds are anomalously low in energy. This can be explained in terms of an electron in the residual NO and NO₂ radicals being converted into a binding electron. Thus whereas in R—N=O there is a double bond between N and O, the NO bond in the free radical is really a 5 electron bond:N::O: This would make understandable the very low 4 kcal bond in O=N—N=O and the weak 14 kcal bond in O₂N—NO₂.

Similar explanations are consistent with the anomalously low value of $DH^{\circ}(\text{ClO}-\text{Cl})=36$ kcal and the anomalously high $DH^{\circ}(\text{Cl}-\dot{\text{O}})=64$ kcal. From independent considerations one would expect Cl-O

Table 6. Some O—H, C—H, and C—C Single Bond Strengths in Radicals

Species RO—H	.DH° (RO—H) kcal/mole	Species Containing C—H	DH° (C—H) kcal/mole	Species Containing C—C	DH° (C—C) kcal/mole
Ó—H ÓO—H ĊH₂O—H ĊOO—H	102 47 31 12	ĊH ₂ —H ĊH—H Ċ—H ĊH ₂ CH ₂ —H	.106 106 81 39	ĊH₂—CH₃ ĊH₂CH₂—CH₃ (ĊH₂)₃C—CH₃ CHCH—CH₃	96 25.5 51 32
		ĊO—H	22 19	CH ₃	27.5 35
		ĊНСН—Н	43	CH ₃	11.5
		ĊC—H COCH₂—H CH₂CO—H allyl	~125 43.5 36 60	$(CH_3)_2C(\dot{C}H_2)$ — CH_3 $\dot{O}CH_2$ — CH_3 $(CH_3)_2C(\dot{O})$ — CH_3 $\dot{C}H_2CO$ — CH_3	20 12 7 30
		Ç-H	40 47.5	$ m OC-CH_3$ $ m \dot{O}_2C-CH_3$	11 -20
		—Н	24		

single bond energies to be in the neighborhood of about 45–50 kcal.

The use of such odd electron bonds makes it unnecessary to discuss allyl radical or benzene molecules in terms of the somewhat vague term, resonance. I feel that it would be preferable to refer to the "stabilization" energy of these species instead. Stabilization of structures by spreading out electrons without reducing total bonding can also explain the curious mystery of why N₂O₃ and N₂O₄ have N—N bonds instead of the expected N—O bonds which are, if anything, expected to be stronger. If we examine the structures of the two forms of N₂O₄, we see that while they have the same total number of binding electrons, the form having the N—N bond has two 3-electron bonds in place of a double and a single bond in the N—O bond form:

A similar argument applies to N_2O_3 . Note that the odd electrons in each case are dative electrons from N to O.

Steric Effects

A popular though still qualitative subject for bond energy considerations is "steric effects." There is a considerable body of evidence to suggest that atoms and groups occupy some "normal" volume of space and that if this volume is restricted in a given molecule, that molecule is made less stable by this crowding.

As an example we may calculate from Tables A-3 and A-4 that $DH^{\circ}(tBu-OtBu)=69$ kcal, significantly lower than the value for the same bond in the less "crowded" tBu-OMe where $DH^{\circ}(tBu-OMe)=78$ kcal. This latter value is fairly representative to within a few kcal (see Table 2) of most alkyl-alkoxy bond strengths. The 9 kcal lowering of the C-O bond energy observed in the tBu_2O is attributed to the repulsion of closely bound bulky tBu groups.

A very similar strain occurs in cis-di-t-butyl ethylene where the heat of isomerization to the strain-free trans compound is 9.5 kcal/mole compared to about 1 kcal/mole for most other cis-trans isomerizations. If we make molecular models of the cis-olefin or the preceding ether with normal bond lengths and angles we find that it is not possible to find a position in which H that it is not possible to find a position in which H atoms from the two close-lying t-butyl groups are not atoms from the two close-lying that distances should correspond to 2.2 Å separation.

A much more striking example occurs in the classical case of hexaphenyl ethane, $C_2\Phi_6$. The C—C bond strength in this compound I have estimated to be about 15 kcal in the gas phase; it is observed to be 11 ± 1 Kcal in various solvents. This can be compared to a kcal in various solvents. This can be compared to a value of 88 kcal in C_2H_6 and 67.5 kcal in hexamethyl ethane. The lowering of about 53 kcal calculated releative to $C_2(CH_3)_6$ must be attributed partly to resoance in the triphenyl methyl radicals and partly to steric nance in the bulky phenyl groups in the parent $C_2\Phi_6$.

The amount of each can be computed by comparing the C—H bond energies in isobutane, $DH^{\circ}[(CH_3)_3C-H] = 91$ with that in triphenyl methane, $DH^{\circ}(\Phi_3C-H) = 75$ kcal.

The difference between these two values of 16 kcal can be ascribed to resonance energy in the $\Phi_3 C \cdot$ radicals. It is very close to the 13–14 kcal of resonance energy calculated for the benzyl radical. The fact that it is not significantly higher than the benzyl resonance energy has been attributed to steric inhibition of resonance. In order for two phenyl radicals to be in conjugated resonance with each other through the central C atom, they would have to be planar as in the following:

However the adjacent ortho H atoms in such a planar structure would have to be almost superposed, a physical impossibility. We must conclude that two such bonded phenyl groups must have their planes at an angle to each other. This is consistent with X-ray diffraction work on solid diphenyl methyl type compounds which have shown an angle of 45–90 between adjacent phenyl planes.

Ascribing 16 kcal of resonance to each of the two Φ_3C -radicals makes a total of 32 kcal resonance energy contribution to the bond weakening in $C_2\Phi_6$ and thus leaves about 21 kcal for steric repulsion of adjacent phenyl groups.

We have deliberately chosen these quite considerable steric effects in $C_2\Phi_6$ and tBu_2O to emphasize the existence of such effects. Many examples of bond weakening have been attributed to steric effects but the magnitudes have been only a few kcal, hardly enough to distinguish them from zero point energy corrections or other small effects. In general one must be quite wary of trying to interpret small differences in bond energies (see p. 504).

Isoelectronic Sequences

For the chemist, one of the historic hatracks for hanging his facts together has been the periodic table. The advent of quantum chemistry has suggested that within the confines of the periodic table one should look to isoelectronic sequences for closely related properties of substances. These are substances with the same number of electrons. We list in Table 7 the values of the BDE for a number of isoelectronic sequences chosen from among the second-row non-metals. It is particularly striking that all of the triple bond energies lie very close together between 224 and 257 kcal/mole. The double bond energies show a larger spread, ranging from a low of about 109 to a high of 175 kcal. These double bonds seem to fall into two groups, all those with C having high energies while those with N and/or O are low. There also seems to be a similar trend in

Table 7. Single and Multiple Bond Energies in Some Isoelectronic Sequences

Triple Bonds	DH° kcal/mole	Double Bonds	DH° kcal/mole	Single Bonds	DH° kcal/mole	Single Bonds	<i>DH</i> ° kcal/mole
N≡N HC≡CH HC≡N C≡O	226 230 224 257	CH ₂ =CH ₂ CH ₂ =0 O=0 HN=0 HN=NH CH ₂ =NH	$ \begin{array}{r} 163 \\ 175 \\ 119 \\ 115 \\ 109 (\pm 10) \\ (154 \pm 5) \end{array} $	CH ₃ —CH ₄ H ₂ N—NH ₂ HO—OH F—F CH ₃ —Cl NH ₂ —Cl HO—Cl F—Cl	88 58 ± 4 51 38 83 5 (60 ± 6) 60 61	CH ₃ —H NH ₂ —H OH—H F—H CH ₃ —NH ₂ CH ₃ —OH CH ₃ —F CH ₃ —I NH ₂ —I HO—I F—I	104 103 119 136 79 91 108 56 (56) 56 58

the homogroup single bond sequence R-R, the energies falling from a high of 88 in C_2H_6 to a low of 38 in F_2 . In the other sequences listed the trends seem to vary in different fashion. Most surprising is the almost constant value of the R-I bonds listed. The same is true of R-Cl bonds, $DH^{\circ}(CH_3-Cl)$ constituting a striking exception.

It would be hard to find any simple model to account for these values. However from a purely empirical point of view it is worth pointing out that the sequence from CH_3 — CH_3 to F—F was the first indication that a low bond dissociation energy might be expected for F_2 .

Bond Energies in Ionized Species

The practical importance of chemical reactions in water and other polar solvents has given great emphasis to the behavior and properties of ionized species in these systems. However ionic species exist in condensed phases solely by virtue of the very enormous solvation or lattice energies in these media. This is strikingly evident in the change of state of species such as N2O5 which are covalent and monomeric in the vapor state but ionic (NO2+NO3-) in the solid. Similarly PCl₅ is monomeric in the gas and ionic (PCl₄+PCl₆-) as a solid. As a consequence of these strong medium interactions it is very difficult to compare species in different solvents or to consider that ions produced in the gas phase have much in common with ions in a solid or a solution. It would be quite surprising if C₂H₅+ ion produced in a mass spectrometer ionization chamber should resemble in many ways its solvated form.

Table 8. Comparisons of Bond Dissociation Energies (kcal/mole) of Neutral and Singly Ionized Diatomic Species

Homor		Heteronuclear Species ^a				
Neutral	Neutral +1 Cation		+1 Cation			
$\begin{array}{cccc} H_2 & 104 \\ N_2 & 226 \\ O_2 & 119 \\ He_2 & 0 \ (?) \\ F_2 & 38 \\ Cl_2 & 59 \\ Br_2 & 46 \\ I_2 & 36 \end{array}$	$\begin{array}{ccc} {\rm H_2}^+ & 62 \\ {\rm N_2}^+ & 200 \\ {\rm O_2}^+ & 168 \\ {\rm He_2}^+ & 50 \\ {\rm F_2}^+ & > 60 \\ {\rm Cl_2}^+ & 94 \\ {\rm Br_2}^+ & 74 \\ {\rm I_2}^+ & 61 \\ \end{array}$	NO 151 CO 257 HO 102 HC 81 HCl 103 HBr 88 HI 71	N—O+ 251 C—O+ 195 H—O+ 118 H—C+ 85 H—Cl+ 97 H—Br+ 83 H—I+ 70			

 $^{^{\}rm a}$ The plus charge is placed on the atom which appears as a cation in the dissociation products, e.g., N—O $^+$ \rightarrow N + O $^+$.

With these warnings in mind, we can consider some of the very interesting data that have accumulated in recent years on the thermodynamic properties of gas phase ions. Whereas electron deficient compounds such as the boranes were chemical oddities and very reactive they appear to be quite common and stable species in the gas phase. Such species as CH₅⁺ and H₃⁺ have H atom affinities in excess of their more stable and familiar Lewis Bases CH₄ and H₂, respectively.

Table A-9 in the appendix lists a number of ionization potentials for some common elements, molecules and radicals. Using these values and the relevant heats of formation it is possible to calculate "bond dissociation energies," eqn. (1), for a number of singly ionized species. These values are listed together with the values for the uncharged species in Tables 8 and 9.

In considering these values let us first entertain some elementary considerations concerning the relations of ionization potentials of molecules to the *IP* of their component atoms. From the strictly classical point of view of electrostatics one expects that as matter is condensed it should become easier to remove electrons from it. This is in reasonable accord with the facts that removal of electrons from bulk metals (the work function) is easier than from their atoms (ionization potential). The physical basis for such a result is the macroscopic view that in removing charge from an aggregate, the resultant charged species can distribute its net charge over its surface. Consequently, the repulsive self-energy due to this net charge will be less as the surface increases.

Supporting such a view, in the sequence $CH_4 \rightarrow C_2H_6 \rightarrow (CH_3)_3CH \rightarrow (CH_3)_4$, the ionization potentials decrease on the average by about 1 ev for each methyl substituent. This is also the value that one can calculate from the polarizability of the CH_3 group (13), assuming that it is simply polarized by the residual +1 charge on the cation.

An equivalent point of view is that any charged species will induce a dipole in any uncharged species and hence will be attracted to it. We should thus expect the work of removing an electron from a molecule or atom to be less if another species is in its neighborhood. Thus we may note in Table A-9 that the IP of O_2 and all of the halogens are less than the IP of their corresponding atoms O_2 , etc.

However we also note that IP (H₂) is 1.83 ev (42

Table 9. Comparisons of Bond Dissociation Energies (kcal/mole) in Neutral Species and in Their +1 Cations

	Triatomic Species		Polyatomic Species				
CO-O NN-O N-NO OS-O ON-O HO-H HS-H HC-H H;-H	127 CO—O+ 40 NN—O 115 N—NO 115 N—NO 125 OS—O+ 73 ON+—C 119 HO+—I H—OH 90 HS—H ⁴ HS+—H 106 HC+—I <0 H _c —H+ + + + + + + + + + + + + + + + + + +	56 31 155 56 119 142 161 104 127	CH ₃ —H CH ₃ CH ₂ —H NH ₂ —H CH ₃ —Cl CH ₃ —I CH ₃ —CH ₃ CH ₃ —NH ₂ CH ₃ —OH CH ₄ —CH ₂ HC=CH CH ₂ —CH ₂ HC=CH CH ₂ —CH ₃	104 98 103 83 56 88 79 92 163 230 39	$\begin{array}{c} CH_3+-H \\ CH_3CH_2+-H \\ NH_2-H+\\ NH_3-H \\ CH_3+-Cl \\ CH_3+-Cl \\ CH_3+-CH_3 \\ CH_3+-OH_2 \\ CH_3+-OH_2 \\ CH_2+-OH_2+\\ CH_2-CH_2+\\ CH_2-CH_3+-OH_2 \\ CH_$	30 22 18: 12: 5: 6: 40 100 67 16: 22: 7: 11:	

kcal/mole) greater than IP (H). This warns us that molecular considerations of bonding must modify our macroscopic electrostatics. The same deviation occurs for N2 and for CO. In discussing heteronuclear systems such as CO, we should compare the molecular IPwith that for the element having the lowest IP. The IP of CO is greater than either C or O but IP (C) is lower than IP (O) by 2.35 ev and so we will compare IP(CO) with IP (C).

The fact that $IP(H_2)>IP(H)$ is not astonishing when one considers that the two electrons in H2 are mainly concentrated in the region between the two nuclei. In removing one of them we are removing it from a more attracting environment than it finds in a single H atom. We are of course removing it from the repulsive interaction of the second electron but the implication of the above result is that this latter repulsion is not as great as the extra attraction of the second nucleus. When an electron is removed from a bonding region we should always expect such a result.

This provides us with a very simple and direct measure of the status of the outer shell electrons (i.e., valence) in molecules. When their IP exceeds that of the atoms, they are bonding electrons; when the converse is true, they are nonbonding or anti-bonding electrons. On this basis we can classify the outer shell electrons in H2, N_2 , and CO as bonding electrons while those in O_2 and the halogens are not. Comparing the IP of the hydrogen halides with their corresponding halogen atoms, we note that IP (HX) is practically identical with IP (X). Hence the valence electrons in the hydrogen halides must be nonbonding electrons.

If such a point of view is pursued it implies some interesting consequences for bond strengths in the cations. Consider the ionization and dissociation of a homonuclear diatomic molecule A2 to produce A+ + A + e^- . The order of the two processes can be interchanged without affecting the over-all process:

out affecting
$$A - A^{+} + e^{-}$$

$$A - A^{+} + e^{-}$$

$$A - A^{+} + e^{-}$$

$$A + A^{+} + e^{-}$$

$$A + A^{+} + e^{-}$$

$$A + A + A^{+}$$

$$A + A$$

$$A + A$$

Hence by conservation of energy:

we by conservation of energy.
$$IP(A_2) + DH^{\circ}(A-A^+) = IP(A) + DH^{\circ}(A-A) \quad (17)$$

For heteronuclear species A-B, the results are of course the same except that because of the two possible sets of products there is a similar equation for each.

$$IP (AB) + DH^{\circ} (A-B^{+}) = IP (B) + DH^{\circ} (A-B)$$
 (18)
 $IP (AB) + DH^{\circ} (^{+}A-B) = IP (A) + DH^{\circ} (A-B)$ (19)

We can rewrite equation (17) or (18) as:

$$IP (A_2) - IP (A) = DH^{\circ} (A-A) - DH^{\circ} (A-A^+)$$

 $IP (AB) - IP (B) = DH^{\circ} (A-B) - DH^{\circ} (A-B^+)$ (20)

which leads us to our important result: if the ionization potential of the molecule exceeds that of the atom (i.e., a bonding electron is removed) then the bond energy in the cation is less than that in the neutral species. The inverse of course follows at once. The removal of a nonbonding or an anti-bonding electron from a species must strengthen the bonds in the resulting cation.

Perusing the list of ionization potentials in Table A-9 we shall find that these considerations are in good accord with our chemical expectations. In Tables 8 and 9 are listed comparisons of bond energies for a number of netural-cation pairs. We note that for H₂, N₂, and CO the removal of a bonding electron has weakened the resulting bond. In the case of N2 this is much less than might have been anticipated. For NO and O2 the removal of what must have been antibonding electrons has strengthened the residual bond in the cation by an astonishing 100 kcal and 49 kcal, respectively. The halogen bond strengths have all been increased by about 28 ± 6 kcal in X₂+, but since a good part of this consists of polarization energy it appears as though the electrons removed were either nonbonding or only weakly anti-bonding.

Looking at the polyatomic molecules in Table 9 we observe that very large changes in bond energies have occurred only in the alkanes and the alkyl radicals. Ionization of the bonding electrons in the alkanes results in weakening C-H or C-C bonds while ionization of the anti-bonding electrons in the alkyl radicals leads to strengthening of the bonds.

In view of these results it is perhaps somewhat surprising to find that for the alkali metal diatomic molecules, recent data (14) indicate that their ionization potentials are about 0.2 ev (~5 kcal/mole) less than those of the corresponding monatomic elements. As a consequence the BDE are inverted. Thus DHo- $(K_2)-DH^{\circ}(K_2^+) = -6$ kcal/mole. While the bond strengths in the diatomic molecules are already anomalously low and the differences small, this would seem to imply either that only one of the two electrons is a bonding electron or else that the polarization energy of the molecule-ion is compensating the diminished bonding.

Although negative ions are of considerable interest, too, little data is available on electron affinities of molecules to permit useful discussion. In fact except for a few unusual cases, the electron affinities of most molecules are either zero or negative.

Conclusions and Some Applications

The last two decades have witnessed a flourishing of experimental work in the field of bond dissociation energies to the point that a tremendous amount of data exists. Theoretical workers in the field have been active for a much longer time, but the theoretical developments have been on the whole meager. Today there is a great need for a unified theory of chemical bonds capable of yielding quantitative data on bond dissociation energies. Until one exists it is difficult to see how chemistry will ever progress much beyond the stage of being a fundamentally experimental and empirical science.

Still if quantitative theories are lacking, we do have numerous empirical relations which exist between limited sets of BDE, some of which we have discussed. One very important relation which does exist for all but the very small molecules is the "Law of Additivity of Group Properties." Benson and Buss (B-1) have shown that large molecules can conveniently be divided into groups in such a fashion that any molecular property can be obtained with good precision by adding up the value for it assigned to each group. A group is defined as any polyligated atom plus its near neighbor atoms. Thus all of the non-cyclic paraffin hydrocarbons can be composed from four groups, a C atom bound to a C atom and 3 H atoms, symbolically C-(C)(H)3, and $C-(C)_2(H)_2$; $C-(C)_3(H)$ and $C-(C)_4$. Assigning these the standard partial molal enthalpies -10.08. -4.95, -1.48, 1.95 kcal/mole, respectively, one can predict the standard heats of formation of all the noncyclic alkanes with excellent precision, generally better than ± 1 kcal/mole.

Ethane, C_2H_6 , for example, consists of 2 C—(C)(H)₃ groups each with -10.08 kcal/mole partial molal heat of formation giving $\Delta H_f^{\circ}(C_2H_6) = -20.16$ kcal/mole. Isobutane is computed to be 3 C—(C)(H)₃ + 1 C—(C)₃(H) = -31.72 and 2,4,4 trimethyl pentane is 5 C—(C)(H)₃ + 1 C—(C)₂(H)₂ + 1 C—(C)₃(H) + 1 C—(C)₄ = -50.40 - 4.95 - 1.48 + 1.95 = -54.88 kcal/mole. The experimental ΔH_f° for these compounds are -20.2, -32.2 and -53.6 kcal/mole respectively.¹⁴

Although the data are not sufficiently extensive to make a really severe test of such a rule it has worked out reasonably well for radicals. Thus the *n*-propyl

 $(CH_2CH_2CH_3)$ radical contains the groups $C-(C)(H)_2 + C-(C)(C)(H)_2 + C-(C)(H)_3$. Two of these groups occur only in radicals but the third is known from molecular data. From ΔH_f° data on a few chosen radicals it is possible to predict ΔH_f° data and thus BDE for large numbers of related radicals. The evidence so far is very strong that groups such as $C-(C)(C)(H)_2$ are identical in properties to their corresponding molecular groups $C-(C)_2(H)_2$. This would imply that a given bond is affected only by nearest neighbors and not by next nearest neighbors.

One of the major categories of problems for which BDE theories must be the key are the old chemical favorites of stability and the related problem of non-existence of certain compounds. Why for example does not oxygen, like sulfur, exist in the form of rings—O₃, O₄, etc (XVIII)? Why does not nitrogen form aromatic rings—N₄, N₅, N₈, etc. (XIX) with alternating single and double bonds, or 3 electron bonds?

While there is no simple theoretical explanation for the instability of such molecules, we do have adequate reasons from our empirical knowledge of bond energies. Thus single bond energies between O atoms range from 30 kcal in acyl peroxides to a high of 51 kcal in HO—OH. However the total bond energy in O_2 is 119 kcal. Thus no matter what value we assign to an O—O bond, the reaction, cyclohexoxide (XVIII) \rightarrow 3 O_2 is exothermic by at least 51 and possibly 177 kcal. Similarly in converting cyclohexazide (XIX) to 3 N_2 we break 3 N—N single bonds rated at about 56 kcal each and get back 3 pi bonds rated in excess of 70 kcal each. Thus the ring fission is exothermic by \sim 42 kcal. Assigning 37 kcal of "resonance" energy still leaves 5 kcal of exothermicity.

The nonexistence of other attractive molecules such as O=C=C=O may be similarly rationalized in terms of the fact that the decomposition into 2 CO liberates $2H_{\tau}(C=O) \sim 146$ kcal/mole at the expense of a C=C double bond (163 kcal/mole strained 20 kcal by two adjacent double bonds and so worth only 143 kcal (see p. 509).

A last illustration of stability will be taken from the cations. CH₅ and H₃ are unstable while CH₅⁺ and H₃⁺ are both quite stable with respect to the dissociation of either H atoms or H⁺. We note that in order for an H atom to bond to CH₄ we must either create a semi-ion pair CH₄^{+1/2} — H^{-1/2} or else place a bonding C—H electron into the next excited level of a pentavalent C atom. Either process looks energetically very unfavorable. However the addition of H⁺ to CH₄ involves no such separation of charge or promotion of ground state electrons. Very simply it may be looked upon as converting one C—H, 2-electron bond into 2 C—H, 1-electron bonds, a process which we expect to be at least 20 kcal exothermic if based on the bonds in H₂ and H₂⁺ (Table 8). A similar argument can be made for H₃⁺ and H₃.

¹⁴ There are small corrections (see B-1) which can be made for repulsion of non-nearest neighbors in highly branched compounds like 2,2,4 trimethyl pentane to improve the predicted value.

The bonding of the pentavalent C atom in CH5+ may be looked upon as a combination of sp^2 for C atom to three equatorial H atoms, together with a pure "p" orbital bonding via two 1-electron bonds (in each "p" lobe) to the remaining two apical H atoms. The geometry would be that of a trigonal bipyramid, and we note that there is a change in hybridization going from CH4 to CH5+.

While such thermochemical considerations provide a basic yes or no indication regarding chemical stability of compounds, they do not tell us whether such endothermic compounds might exist in special environments since the actual stability of compounds is as much a matter of rate as it is of thermal stability. In the present instances where the decomposition does not require extensive rearrangements of atoms, either intra- or intermolecular, the thermochemical considerations and kinetic ones would probably agree.

Thermochemical and BDE data are an invaluable tool for analysis of kinetic behavior. This is much too extensive a field to discuss in detail here. However two illustrations from recent work may be useful. HI and DI are extraordinarily effective scavengers (15) for free radicals, but perhaps their greatest advantage lies in the fact that radicals can abstract only the H or D atoms, thereby forming quite stable products and leaving behind the very inert I atoms.

The reason for this apparently unique behavior is that the H-I bond is the strongest bond that I forms with any species and practically the weakest that H forms with any species. Consequently the reaction $I-H \rightarrow R-I+H$ is always endothermic. The endothermicity of the latter reaction is so large that it effectively never occurs relative to the former.

Our other example concerns the relation between the kinetic behavior of molecules with low energy and high energy radiation. Recent work in radiation chemistry (16) and for UV photolysis (17) of organic molecules indicate that H atoms are important species in these systems. In contrast, thermal pyrolysis of organic molecules and near UV (low energy) photolysis produce mainly alkyl and other large radicals. If we choose C_2H_6 as a specific example, we may note that a C_2H_6 molecule, excited thermally, will preferentially break into 2 CH3:

$$C_2H_6$$
 -88 kcal (XX)
$$H + C_2H_6 -98 \text{ kcal}$$

That is, the equilibrium—H + $C_2H_6 \rightleftharpoons 2$ CH3 + 10 kcal—favors the production of CH₃ radicals.

On the other hand an excited (C2H6+)* ion such as might be produced by ionizing radiation or an electron collision in a mass spectrometer will dissociate preferentially into C_2H_5++H (see Table 9):

i.e.,
$$\mathrm{CH_8} + \mathrm{CH_3}^+ \! \to \mathrm{C_2H_6}^+ + \mathrm{H} + 17$$
 kcal.

This can be generalized to most large alkanes, ethers, and ketones. If we consider the very large energy associated with the vacuum ultraviolet ($\lambda < 2000 \text{ Å}$) as producing electrons in very high energy states, then it is probably fair to consider that the molecules containing such highly excited electrons will behave more nearly like molecules that are ionized rather than like molecules which are vibrationally excited only. It is then reasonable to expect them to act like the cations rather than like the neutral species.

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Annotated Bibliography and Data Source

This is a very carefully screened bibliography chosen for coverage and exposition. In general, duplication has been avoided.

- (B-1) Benson, S. W., and Buss, J. H., "Additivity Rules for the Estimation of Molecular Properties, Thermodynamic Properties," J. Chem. Phys. 29, 546 (1958). 26
 - A discussion and unification of molecular additivity laws with special application to thermochemical data, Cp°, S° and ΔH,° for ideal gases at 25°C. Lists tables of values which can be used to estimate these quantities for complex molecules of known structure to within small limits of uncertainty. Discusses relation to BDE.

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(B-2) COTTRELL, T. L., "The Strengths of Chemical Bonds."
2nd ed., Butterworths Scientific Publ., London, Eng-

land, 1958, 316 pp.

The most extensive of the recent compilations of BDE. These are not always critical. They are best for small molecules. Has excellent discussion of methods of measuring ΔH_f° of molecules and very brief summary of methods of measuring BDE. Latter is extensive on more esoteric methods such as explosions, high temperature spectroscopic and kinetic.

Level: senior and graduate.

(B-3) FIELD, F. H., AND FRANKLIN, J. L., "Electron Impact Phenomena and the Properties of Gaseous Ions,' Academic Press, New York, 1957, 349 pp.

An excellent review of mass spectrometric methods for the measurements of BDE, ionization potentials and ion-molecule reactions in gases. Has extensive tables of IP, BDE and heats of formation of ions (positive and negative) and radicals from both mass spectrometric and spectroscopic measurements. Level: junior or senior.

(B-4) GAYDON, A. G., "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed., Chapman and Hall, Ltd., London, England, 1953, 239 pp.

Extensive discussion of optical spectroscopy of diatomic molecules and its relation to potential energy curves and BDE. Has good brief discussion of methods for measuring BDE. Many values quoted are in error.

Level: senior or graduate, depending on physics background.

(B-5) Gray, P., and Williams, A., "The Thermochemistry and Reactivity of Alkoxy Radicals," Chem. Rev., 59, 239 (1959). 89 pp.

An excellent survey of the available thermochemistry of organic oxygen compounds and the radicals derived from them. They also include discussion of the kinetics of decomposition of these radicals and the relation of the kinetics to BDE.

Level: junior and senior.

(B-6) Green, J. H. S., "Thermodynamic Properties of Organic Oxygen Compounds," Quart. Rev., 15, 125 (1961). 27

The most recent critical review of the heats of formation and heats of vaporization of organic compounds containing oxygen.

(B-7) JANAF Interim Thermochemical Tables (1960-1965). Issued from the Thermal Laboratory of the Dow

Chemical Co. at Midland, Michigan.

Tables of values of ΔH_f , C_p , S_p , and $\log K_f$ for several hundred substances (gas, solid, and liquid) at 100°C intervals over the range 0-1500°K and 0-6000°K. These are the most comprehensive and generally reliable tables of such data now available. They are carefully annotated to give references for all data and uncertainty limits are carefully evaluated. They also give structural data and spectroscopic (infrared) frequency assignments for molecules treated.

(B-8) Janz, G. J., "Estimation of Thermodynamic Properties of Organic Compounds." Academic Press, Inc., New

A critical compilation (prior to Benson and Buss) of the various methods for estimation of thermodynamic data, C_p °, S°, ΔH_f °, and ΔH_{vap} of organic molecules. Gives tables for estimating these quantities over the temperature range 0-1500°K.

(B-9) Kerr, J. A., and Trotman-Dickenson, A. F., "Strengths of Chemical Bonds," Chemical and Rubber Handbook, 45th ed., Chemical Rubber Co., Cleveland, Ohio, 1964, p. F-94.

A generally reliable and very recent compilation of BDE and ΔH_f ° for some radicals.

(B-10) Moelwyn-Hughes, E. A., "Physical Chemistry," 2nd ed., Pergamon Press, New York, 1961.

One of the currently outstanding works in physical chemistry emphasizing the molecular point of view. Contains excellent short discussions of BDE (Chap.

XX) and the spectroscopy of diatomic molecules (Chap. X).

Level: graduate and advanced senior.

(B-11) MORTIMER, C. T., "Reaction Heats and Bond Strengths," Pergamon Press, New York, 1961, 230 pp.

A very readable and extensive discussion of bond energies and heats of reaction and their relation to the structure of organic molecules. Emphasis is on heats of hydrogenation of unsaturates, heats of polymerization. Includes discussion of metal organies: metal halides; ionization of weak acids in aqueous solution; and silicon, phosphorus, and sulfur compounds. Has good discussion of resonance and steric effects.

Level: junior and senior.

(B-12) Pauling, L., "Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, 644

Historically one of the major works on chemical bonds and their relation to structure. However, emphasis is on DH^a which diminishes its use in discussing BDE.

Level: senior.

(B-13) Reid, R. C., and Sherwood, T. K., "The Properties of Gases and Liquids, Their Estimation and Correlation," McGraw-Hill Book Co., Inc., New York, 1960.

This is probably one of the most useful books available for the estimation of physical and thermodynamic properties of gases, liquids, and solids over extended temperature ranges. They compile and compare most of the empirical relations known together with their limits of uncertainty.

(B-14) STEACIE, E. W. R., "Atomic and Free Radical Reactions," 2nd ed., Vol. 1. Reinhold Publishing Corp., New York, 1954.

Chap. 3 (24 pp.) contains one of the earliest, reasonably simple and comprehensive discussions of BDE and the uncertainties of different methods for measuring them. Emphasis is on kinetic and mass spectroscopic methods.

Level: junior and senior.

(B-15) Skinner, H. A., "Thermochemistry and Bond Dissociation Energies," Ann. Rev. Phys. Chem., 15, 449 (1964).

Survey of current work in the field during 1962-63. Level: graduate.

(B-16) SEHON, A. H., AND SZWARC, M., "Bond Energies," Ann. Rev. Phys. Chem., 8, 439 (1957). 23 pp. Survey of work in the field during 1954-56.

Brings much of Szwarc's earlier review (B-17) up to date.

Level: Graduate.

(B-17) Szwarc, M., "The Determination of BDE by Pyrolytic Methods," Chem. Rev., 47, 75 (1950). 98 pp.

The first critical survey and compilation of BDE. Contains an excellent discussion of the various experimental methods and their difficulties. Discusses also DH^a and DH^o . Gives an extremely detailed examination of kinetic methods with emphasis on the toluene "carrier" technique. This latter is not as reliable as claimed.

Level: senior or graduate.

(B-18) "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, U. S. Government Printing Office, Washington 25, D. C., 1952.

Contains values of C_p °, S°, ΔH_f ° at 25°C for elements, ions, aqueous solutions of compounds and gases for all compounds to date of printing. Gives original literature references. Is not uniformly

(B-19) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Inst. Res. Proj. #44, Carnegie Press, Pittsburgh, Pa., 1953.

One of the most extensive and critical compilations of physical and thermodynamic data on hydrocar-

bons over the range 0-1500°K.

Appendix

The following tables (A-1 through A-9) contain ΔH_f^0 in keal/mole and ionization potentials (*IP*) in electron volts for molecules, atoms, and radicals in the ideal gas state. The limits of uncertainty are usually ± 1 kcal for ΔH_f^0 unless otherwise stated. For values given to 0.1 of a kcal or 0.01 of a kcal the uncertainty is usually in the last significant figure.

A number of BDE are determined directly from spectroscopic or other methods in the absence of good ΔH_f ° for reactants or products. In such cases DH^0 is known better than ΔH_f^0 for reactants and products and the combined error limit on the latter may even exceed DH^0 .

The values listed are generally from the data sources given in the bibliography. In a number of cases I have estimated values or corrected values at my own discretion to agree with data from independent or unpublished sources.

Table A-1. Standard Heats of Formation of Some Monatomic Elements in the Ideal Gas State^a

Element	ΔH_f°	Element	ΔH_f°
Н	52.1	Cl	28.9
D	53.0	K	21.3
D Be	78.3	Ca	46.0
	$133(\pm 4)$	Cu	81.5
C	170.9	Zn	31.2
N	113.0	Ge	78.4
ô	59.6	Br	26.7
F	18.9		
B C N O F Na	25.8	Ag	69.1
	35.3	Sn	72
Al	78.0	Sb	60.8
Si	$106(\pm 4)$	I	25.5
P	79.8	Hg	14.7
Mg Al Si P S	65.7	Pb	46.7

 $^{\circ}$ All values in this and following tables are in kcal/mole. Uncertainties are less than \pm 0.5 kcal for values given to tenths of kcal. All others are \pm 1 kcal unless noted otherwise.

Table A-2. ΔH_f° of Some Diatomic Molecules in the Ideal Gas State

	• *************************************	2. Δη, οι σειιιτ	———Heteronucl	ear species—	
120	-lear species	Hydrides and oxides	$\Delta H_f{}^o$	Misc.	$\Delta H_f{}^0$
Homonu B ₂ C ₂ Na ₂ Si ₂ P ₂ S ₂ K ₂ Cu ₂ Br ₂ Ag ₂ Sb ₂ Pb ₂	clear species ΔH_f^0 $195 (\pm 6)$ $199 (\pm 2)$ 32.9 $311 (\pm 5)$ 42.7 30.8 30.4 $117 (\pm 3)$ 7.4 $100 (\pm 3)$ 52 $80 (\pm 5)$	HF HCI HBr HI HNa KH BeO CO NO MgO SiO	$\begin{array}{c} -64.8 \\ -22.0 \\ -8.7 \\ 6.3 \\ 29.7 (\pm 5) \\ 29.4 (\pm 3.5) \\ 31 (\pm 3) \\ -26.4 \\ 21.58 \\ 4 \\ -24.2 (\pm 1) \end{array}$	BC BN NP FCI FBr FI CIBr CII BrI NaF NaCI NaBr NaI CuCI AgCI	$\begin{array}{c} 198 (\pm 10) \\ 152 (\pm 12) \\ 24 (\pm 1.2) \\ -13.5 \\ -14.0 \\ -13.9 \\ 3.5 \\ 4.1 \\ 9.7 \\ -70 (\pm 2) \\ -43.4 \\ -34.4 \\ -20.4 \\ 32 \\ 23 \end{array}$

Table A-3. ΔH_f° of Some Triatomic and Tetratomic Molecules in the Ideal Gas State

Table A-4. ΔH_f° for Some Polyatomic Inorganic Molecules in the Ideal Gas State

able .	In life idea.		
	ΔH_f°	Species	$\Delta {H_f}^{\circ}$
Species N ₂ O ₃ N ₂ O ₄ N ₂ O ₅ HNO ₃ N ₂ H ₄ NH ₂ OH N ₂ F ₄ POCl ₅	$\begin{array}{c} \Delta H f \\ 19.8 \\ 2.2 \\ 2.7 (\pm 0.3) \\ -32.1 \\ 22.8 \\ -8 (\pm 1) \\ -2 (\pm 2.5) \\ -81.9 (\pm 1) \\ -19.6 \\ 8.6 (\pm 3) \end{array}$	S ₈ CCl ₄ CF ₂ Cl ₂ CF ₄ C ₂ F ₄ Al ₂ Cl ₅ SiCl ₄ IF ₅ IF ₇ SiF ₄	$\begin{array}{c} 24.2 \\ -26.0(\pm 2) \\ -112(\pm 2) \\ -221(\pm 3) \\ -155(\pm 2) \\ -309.2 \\ -157(\pm 2) \\ -200(\pm 2) \\ -229(\pm 2) \\ -386.0 \end{array}$

Table A-5. ΔH_f° for Some Hydrocarbons in the Ideal Gas

Species	ΔH_f°	Species	ΔH_f°
CH ₄ C ₂ H ₄ C ₂ H ₆ C ₃ H ₆ C ₃ H ₈ i-C ₄ H ₁₀ neo-C ₅ H ₁₂ butene-2,cis butene-2,trans allene butadiene isoprene	-17.9 12.5 -20.2 4.9 -24.8 -32.2 -39.7 -1.7 -2.9 45.9 26.3 18.1	cyclopropane cyclobutane cyclopentane cyclopentane cyclopentane methyl cyclopentane methyl cyclohexane cyclobutene cyclopentene cyclopentene toluene styrene biphenyl (C ₆ H ₅) ₂ CH ₂ (C ₆ H ₅) ₂ CH	$\begin{array}{c} 12.7 \\ 6.3 \\ -18.5 \\ -29.5 \\ -25.5 \\ -37.0 \\ 35 (\pm 1) \\ 7.9 \\ -0.9 \\ 19.8 \\ 12.0 \\ 35.2 \\ 42.6 \\ 32.6 \\ 60 (\pm 2) \end{array}$

Table A-8. ΔH_f° of Some Polyatomic Free Radicals in the Ideal Gas State

Species	ΔH_f°	Species	ΔH_I°
CCl ₁ CF ₃ NO ₃ CH ₄ C ₅ H ₅ -C ₅ H ₇ -C ₆ H ₇ -C ₆ H ₇ -C ₆ H ₉ CH ₂ =CH—CH ₂ c ₆ H ₅ -c ₇	$18.5(\pm 1)$ $-113(\pm 2)$ $17.0(\pm 1.5)$ $34.0(\pm 1)$ $26.0(\pm 1)$ $17.6(\pm 1)$ $6.7(\pm 0.7)$ $38(\pm 1)$ $63(\pm 2)$ $71(\pm 2)$ $45(\pm 1)$ $13(\pm 1)$ $55(\pm 2)$ $29(\pm 1)$ $49.4(\pm 2)$	CH ₃ O CH ₃ NH C ₂ H ₅ O C ₂ H ₅ O ₂ C ₆ H ₅ O t-C ₄ H ₉ O CH ₁ OCH ₂ CH ₄ CO COOH CH ₃ COCH ₂	$\begin{array}{c} 2(\pm 2) \\ 35(\pm 2) \\ -6(\pm 1) \\ -2(\pm 2) \\ 10(\pm 3) \\ -24.7(\pm 1) \\ -4.0(\pm 1) \\ -54(\pm 3) \\ -11(\pm 2) \end{array}$

Table A-6. $\Delta H_f^{\,\circ}$ of Some Polyatomic Organic Molecules in the Ideal Gas State

CH₂F	Compounds		Oxygen C	Organic Molecul			
CH4CI CH4Br CH4CI CH4F2 CH4F2 CH4F2 CH4F3 CHCI CHF4 CHCI CH4F CHCI CH4F CHCI CH4F CHCI CH4F CHCI CH4F CHCI CH4CI CH4F CH4CI CHCI CH4COF CH4COF	$\begin{array}{c} -55 (\pm 2) \\ -20.7 \\ -9.5 (\pm 1) \\ 3.3 \\ -22.4 (\pm 4) \\ -107.2 (\pm 1) \\ +26 (\pm 2) \\ -165 (\pm 2) \\ -25.0 (\pm 1) \\ -61 \\ -26.7 \\ -16.3 \\ -2.1 \\ 8.1 \\ -104 \\ -31.5 \\ -58.9 \end{array}$	CH ₃ OH CH ₃ CH ₂ OH CH ₂ CH ₂ OH t-C ₄ H ₂ OH t-C ₄ H ₂ OH CH ₂ CH—CH ₂ OH CH ₂ CH ₂ OH tCH ₂ OCH ₃ tC ₄ H ₃ OCH ₄ tCH ₂ OCH ₃ t-C ₄ H ₃ OCH ₄ t-C ₄ H ₄ OCH ₄ t-C ₄ H ₃	-48.1 -56.2 -65.2 -74.7 -30.2 -23.1 -23.1 -92.8 -44.0 -60.3 -70.0 -87(?) -12.2 -22(?)	dioxane 1,4 CH ₂ (OCH ₃) ₂ C ₆ H ₅ OCH ₃ C ₆ H ₅ OCH ₃ CH ₄ OCCH ₃ CH ₄ OOCH ₃ CH ₄ OOCH ₃ CH ₅ OCH ₅ CH ₅ OOCH ₄ CH ₅ OOH CH ₅ COCH ₃ CH ₅ COCH ₄ CH ₅ COOH CH ₅ COOCH ₄	$\begin{array}{c} -76.0 \\ -79 (\pm 3) \\ -19 \\ 6.1 \\ -32 \\ -48 \\ -40 \\ -39.7 \\ -51.8 \\ -58 \\ -6 (\pm 3) \\ -15.0 \\ -88.5 (\pm 2) \\ -103.8 \\ -175 (\pm 5) \\ -83.6 \\ -99 (\pm 1) \\ -78.1 \\ -24 (\pm 1.5) \end{array}$	N and S Cor CH ₁ NH ₂ (CH ₂) ₂ NH C ₂ H ₄ NH ₂ C ₆ H ₄ NH ₂ C ₆ H ₄ NN C CH ₁ CN CH ₁ NC CH ₂ CH—CN NC—C≡C—CN CH ₂ NO CH ₄ SON CH ₄ SSCH ₃ CH ₄ SSCH ₃ CCH ₄ SSCH ₄	$\begin{array}{c} \text{npounds} \\ -5.1 \\ -4.5 \\ -11.6 \\ 20 \\ 36 \\ 43.7 \\ 127.5 \\ 15 (\pm 1. \\ -22.2 \\ -15.0 \\ -28.0 \\ -32.3 \\ -5.5 \\ -6.9 \\ -5.7 \end{array}$

Table A-7. ΔH_f° of Some Diatomic and Triatomic Free Radicals in the Ideal Gas State

TTO			Diatomic		ree Radicals in the Ide	al Gas Stat	е
HO DO HC HN HB HB HS HAI HHg	$\begin{array}{c} 9.3 \\ 8.4 \\ 142 \\ 79.2 \\ 106 (\pm 2) \\ 33 (\pm 2) \\ 62 (\pm 5) \\ 57 (\pm 4) \end{array}$	BO AlO SO ClO PO BC CS CN	$\begin{array}{c} 6 \left(\pm 10\right) \\ 21 \left(\pm 2\right) \\ 0.5 \\ 24.2 \\ -1.5 \left(\pm 2\right) \\ 198 \left(\pm 10\right) \\ 55 \left(\pm 5\right) \\ 109 \left(\pm 3\right) \end{array}$	BeF BeCl BF BCl CF MgF AIF AICl AIBr HgCl	$\begin{array}{c} -50 (\pm 2) \\ 3 (\pm 3) \\ -28 (\pm 3) \\ 34 (\pm 4) \\ 74.4 \\ -53.1 (\pm 1.3) \\ -62.5 \\ -11.2 \\ 3.6 (\pm 5) \\ 19 (\pm 2) \end{array}$	C ₃ HO ₂ CH ₂ NH ₂ CHO NF ₂ CF ₂ Al ₂ O	Triatomic $ \begin{array}{c} 190 (\pm 3) \\ 5.0 (\pm 2) \\ 88 (\pm 3) \\ 40 (\pm 2) \\ 6.3 (\pm 2) \\ 10.0 (\pm 1.3) \\ -30 (\pm 10) \\ -31.4 (\pm 2) \end{array} $

Table A-9. Ionization Potentials of Some Atomic, Radical, and Molecular Species^a

Elements H 13		Diatomic Species	Mole	cules	Jular Species ^a	
C 11. N 14. He 24. Ar 15. O 13. S 10. F 10. IT 17. Cl 17. L 18. I 10. K 10. K 4. Mg 5. K 4. Mg 5. 7.	54 O ₂ 58 F ₂ 76 CI; 61 Br. 36 I ₂ 42 CH 01 OH 84 HC 44 HB 30 HI 55 CO 14 NO	15.6 12.1 16.5(?) 11.5 2 10.6 9.3 11.1 12.8(?) 21 12.74 31 12.8(?) 31 12.74	CH ₄ C ₂ H ₆ C ₂ H ₄ C ₂ H ₂ NH ₃ C ₄ N ₂ HCN H ₂ O H ₂ S CH ₃ I CO ₂ N ₂ O NO ₂ SO ₂ CH ₃ OH CH ₃ NH ₂	13.0 11.7 10.5 11.4 10.15 13.6 13.9 12.59 10.46 9.6 13.79 12.90 12.0 12.34 10.85 8.97	CH ₂ CH ₃ C2H ₄ C2H ₅ C2H ₆ NH ₂ HO ₂ <i>t</i> -Butyl CH ₄ CO HCO	10.3 9.9 9.7 11.3 11.5 6.9 7.9 8.8(?)

NEW DEMONSTRATION EXPERIMENTS ILLUSTRATING DISPLACEMENTS OF CHEMICAL EQUILIBRIUM

by

Tomonari Nishikawa

A. Background and Summary of this Experiment.

The nitrogen dioxide experiment is usually used to show changes of equilibrium in gaseous systems. When the change of volume of nitrogen dioxide with increase of pressure is measured, the decrease of the volume observed is more than that expected from Boyle's law, and when the change of pressure with increase of temperature is measured, the increase of pressure observed is twice as large as that expected from the Boyle-Charles law. The objects of the new demonstration experiments proposed here are to determine the increase or decrease of the number of molecules directly from measurements of the changes of volume and pressure of nitrogen Since the increase or decrease of the number of molecules is closely related to the general principle of the change of equilibrium, it is important to pay attention to the change of the number of molecules.

Nitrogen dioxide is a suitable material for these experiments, since the equilibrium of a nitrogen dioxide system changes fairly rapidly at room Simple equipment only is used so that results of high precision cannot be expected. Nevertheless, the objects of these experiments are fully accomplished with this equipment.

Change of Equilibrium with Pressure. B.

1. Apparatus.

Fig. 1 shows the apparatus used. (1) and (2) are vacuum The burette attached to (2) is an eudiometer. (4) is an empty polyethylene bottle commercially available as a mayonnaise thylene politic of the glass bottle containing this

The rubber stopper of the glass bottle containing this Polyethylene bottle is fastened with metal wire. (6) is a polyethylene bag attached to a glass tube, which functions as a temporary waste gas

reservoir so as not to contaminate the air in the room.

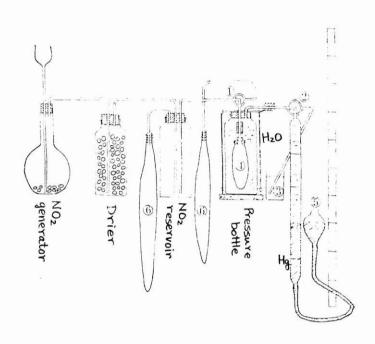


Figure 1

In this experiment, nitrogen dioxide is compressed in a polyethylene bottle. Since mercury reacts rapidly with nitrogen dioxide and oil forms a green solution with nitrogen dioxide, neither of these can be used for applying pressure to nitrogen dioxide.

After the apparatus is assembled, it is adjusted as follows. The air bubbles in a cavity between the pressure bottle and the burette are removed. A slight pressure is applied to the polyethylene bottle, and the reading of the mercury level is set to zero by adjusting the amount of water used for applying pressure to the polyethylene bottle. If water should get into the polyethylene bottle, or air bubbles should come out, the bottle should be

2. Measurements.

(a) Measurements using air.

The stopcock (1) is opened, the mercury level is lowered to the 30 ml line of the burette, and stopcock (1) is closed. Then the mercury reservoir (5) is elevated by 70 cm from the original position, and the height of the mercury level is read. This operation can be repeated many times.

(b) Measurements using nitrogen dioxide.

Nitrogen dioxide is generated, and transferred to the reservoir (6). By proper handling of (1) and (5), the air in (4) is replaced by nitrogen dioxide as completely as possible. Thus, nitrogen dioxide of volume equal to that of the air is enclosed, and the compression and expansion of the gas is repeated as in the case of air. It is inevitable that some nitrogen Therefore, the average of the volume before compression and the volume after compression and immediate release is regarded as "the volume before compression".

The experiment shows that nitrogen dioxide is apparently compressed to a greater extent than air under the same condition.

3. Study guidance.

This experiment deals with nitrogen dioxide and air under the Similar conditions, and therefore, without complicated calculations, one can recognize that nitrogen dioxide is compressed to a greater extent than Moreover, the results obtained are similar to those expected from the mass action law.

Before any demonstration experiment clearly The experiment clearly before any demonstration capetiment clearly. The objects of to show students the objects of the number of molecules in the this this experiment are to see whether the number of molecules in the system increases or decreases with increase of pressure, and whether or not the composition or the equilibrium of the system changes upon increase of pressure, provided that students have learnt the equilibrium $2NO_2 \longrightarrow N_2O_4$.

If the If this experiment is regarded as an application of mass action law, students should predict the change of the number of molecules by compression before the compression of the number of molecules by compression before the compression of the number of molecules by compression before the compression of the number of molecules by compression before the compression of the number of molecules by compression before the compression of the number of molecules by compression before the number of molecules by compression by the number of molecules by the number of mo the experiment. As for Le Chatelier's principle, it is interesting that this experiment shows that the decrease of the volume upon compression is many hat the uecrossion that the results are except. if sufficient preparation is made, and the results are easy to interpret.

4. Results and discussion.

The results of this experiment obey the mass action law. Table 1 shows the results of one experiment. These are rewritten in Table 2 using absolute values of pressure and volume. These absolute values of pressure are the values calculated from the transfer of mercury and water in the burette (8.5 cm per 10 ml). The values of the original volume are obtained from the volume change of air with pressure using Boyle's law, and correspond to the volume of Table 1 corrected for the volume of the cavity of (4) at the zero level of mercury. The initial volumes of experiments 2, (a), (b), (c) differ one another due to the decrease of NO₂, but in Table 2 they are standardized to the initial volume of (a).

	Table	1				
Expt. number	1	us.	2	(a)	(b)	(c)
Temperature (°C.)	30	30	27	27	27	27
Gas	air	NO_2	air	NO_2	NO_2	NO2
Initial mercury height (cm)	76	76	76	76	76	76
Initial volume reading (ml)	30.5	30.3	39.6	38.8	38.0	37.9
Mercury height at increased pressure (cm)	70	70	70	70	50	20
Volume reading at increased pressure (ml)	11.5	10.5	18.6	17.3	21.3	30.0

Table 2

Expt. number	1		2	(a)	(b)	(c)
Temperature (°C.)	30	30	27	27	27	27
Gas	air	NO_2	air	NO_2	NO_2	NO_2
Initial pressure (cm Hg)	76	76	76	76	76	76
Initial volume (ml)	45.2	25.0	50.8	50.0	50.0	50.0
Pressure when increased (cm Hg)	131.0	130.4	129.4	129.0	112.7	89.7
Volume at increased pressure (ml)	26.2	25.2	29.8	28.5	33.0	42.0
Volume by Boyle's law at increased pressure (ml)	26.2	26.2	29.8	29.5	33.7	42.4
Decrease of volume (ml)	0.0	1.0	0.0	1.0	0.7	0.4

The decrease in volume caused by the change of equilibrium is clearly shown in Table 2. However, the values are relatively small compared with the total volume of the experiment. This decrease of volume can be compared the total volume of the experiment. This decrease of volume can be compared the total volume of the experiment. With the pressure equilibrium constant. With the theoretical value calculated from the pressure equilibrium constant. With the theoretical value calculated from the pressure equilibrium constant. The calculation is as follows. The dissociation of N_2O_4 is 20% at 27° and The calculation is as follows. From these handbook values, the value at 30°C is 40% at 50° C at 1 atm. From these handbook values and the dissociation calculated to be 22%. Then, the partial pressures and the dissociation constant are calculated.

calculated.
$$P_{N_{2}O_{4}} = 48.6 \qquad P_{NO_{2}} = 27.4 \text{ (cm Hg)}$$

$$P_{N_{2}O_{4}} = (P_{NO_{2}})^{2}/P_{N_{2}O_{4}} = 15.46$$

$$K_{p} = (P_{NO_{2}})^{2}/P_{N_{2}O_{4}} = 15.46$$

If the partial pressure of NO $_2$ at the total pressure of 130.4 cm Hg is represented as X cm Hg,

$$x^2/(130.4-X) = 15.46$$

 $x = 37.9 \text{ cm Hg}$

The partial pressure of NO_2 is then 130.4 - 37.9 = 92.5 cm Hg. The volume after the compression, V, can be calculated by the comparison of PV before and after the compression.

$$(27.4 + 48.6 \times 2)$$
 45.0 = $(37.9 + 92.5 \times 2)$ V

V 3 25.1 ml

This value is approximately the same as the value obtained by the experiment 1 in Table 2, which is 25.2 ml.

The nitrogen dioxide used in this experiment is generated from copper and concentrated nitric acid, and the purity is not high so that the results are not of superb quality. Nevertheless, this experiment can be used as a quantitative experiment to demonstrate the displacement of equilibrium.

C. Change of Equilibrium with Temperature.

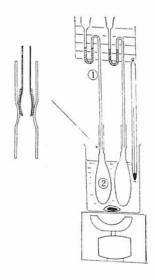


Figure 2.

1. Apparatus.

The gas container (2) (Figure 2) has a volume of about 30 ml and is made by blowing a glass tube. The use of this container enables small scale apparatus to be used and shorter rubber connections because of the narrow mouth.

The glass tubing (1) must be narrow and long so that the volume change due to the change of mercury level is minimum and the mercury is well separated from nitrogen dioxide. The lower end of the tubing is slightly expanded, covered with a rubber tubing, coated with vaseline, and pressed on the inner mouth of the container (2). Theoretically it is better to do this experiment under conditions of constant pressure, but in order to keep the apparatus as simple as possible approximately constant volume conditions are used. The actual volume of container (2) is 33 ml and the inner diameter of the glass tubing is 2 mm. Therefore, the increase of volume with the change of mercury level is less than 1/10 of the value in the case of constant pressure expansion.

2. Operation.

First, both containers are filled with air, and placed in a beaker with cold water, to which hot water is slowly added. One can observe that the rise of mercury levels is similar in the both tubings.

Then the hot water in the beaker is replaced with cold water, one container is filled with nitrogen dioxide, and hot water is slowly added to the beaker with stirring. The rise of the mercury level with nitrogen dioxide is more than twice that with air. Since the expansion of nitrogen dioxide is rapid, mercury may be blown off if hot water is added too rapidly.

The mercury level is not expected to resume the original position even if the container is cooled with ice water, since some loss of nitrogen dioxide is inevitable. Therefore, it is desirable that the nitrogen dioxide should be quickly removed from the container before it rises in the tubing.

If a teacher is familiar with the procedure, this experiment can be completed within 5 minutes.

3. Study guidance.

It is desirable to carry out this experiment at the same time as the experiment on the change of the equilibrium with pressure.

My teaching practice is that if students have previously done the experiment of the colour chan ge of nitrogen dioxide with temperature, this further experiment is shown to them without any special explanation.

The experiment is first carried out using air in order to let students recall Boyle-Charles' law, followed by the experiment with nitrogen dioxide, and the discussion on the results is emphasized. Their thinking is guided so that they may realize that the pressure of a gas depends upon n, V and T in PV = nRT and the factor to cause the difference must arise from the change of n. The experimental results are explained in terms of the change of $N_2O_4 \longrightarrow 2NO_2$ with temperature. Students show far greater interest in this experiment than in other experiments.

It is rather difficult to give a theoretical explanation on the change of equilibrium with temperature, and usually only Le Chatelier's principle is used. However, since the evolution or absorption of heat cannot be measured by simple experiments, the explanation by Le Chatelier's principle cannot be illustrated by a suitable experiment. But the increase of the number of molecules with temperature can be reasonably understood not only in terms of the common sense that stronger vibration of molecules may cause the disruption of molecules, but also in terms of the practical meaning of the increase of entropy. Thus, the implication of this experiment is rather great.

4. An example of the experiment.

Table 3 shows an example of this experiment.

T	able	3

Expt.	Temp. change	Difference	Increase of	f pressure NO ₂	
1	28.0 - 36.8	8.8	9. 0	1102	Difference
1	26.8 - 31.4		2.0	4.2	2.2
	-0.0 - 01.4	4.6	0.9	2.0	1.1

The elevation of mercury level with air at Expt. 1 must be 2.2 cm from Boyle-Charles' law, but the value observed is 2.0 cm. This error is due to the movement of mercury. As for nitrogen dioxide, the elevation of mercury level is expected to be 6.3 cm from the calculation by use of the dissociation constants of N $_2$ O $_4$, 20.9% at

 28°C and 28.5% at 36.8°C (these constants are calculated from the values shown in a handbook, 20% at 27°C and 40% at 50°C). Thus the observed value is rather smaller than the calculated value. The error may be ascribed to the facts that the change of pressure is neglected in the calculation and that the purity of NO_2 is low. Although the error is rather large, this experiment presents very clear results by a simple apparatus, and is significant at least as a qualitative experiment.

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The Dissolution of Tin In Solutions of Iodine

A kinetic experiment

Reactions that can be followed by physical methods offer considerable didactic advantages when used as an introduction to chemical kinetics. Chief among these is that the student can see the progress of the reaction with time. Unfortunately, most physical methods require expensive apparatus, and hence are unsuitable for large classes. Moreover, they usually take an hour or so to set up and adjust before measurements can begin. The dissolution of tin in solutions of iodine in benzene, however, can be set up rapidly, and the apparatus required is widely available. The progress of the reaction can be followed by the loss of weight of a tin disc.

Prepare tin discs about 1.5 cm in diameter and 2 mm thick by casting a bar of tin metal in a clean glass tube. The tin bar can be cut into discs with a small hacksaw or on a lathe. Then drill fine holes through the discs. Each disc should be cleaned with fine emery paper and then handled carefully by the edges. Hang on a thread from the hook of a single pan balance. Monofilament nylon thread is suitable for this purpose. Adjust the length of the thread so that the disc hangs about 1 cm below the surface of 10 ml of iodine solution contained in an open 25 ml. weighing bottle placed on an Archimedian bridge. The disc must hang horizontally, but thermostating is not necessary because the temperature coefficients of diffusion controlled reactions are very low. Benzene is the most suitable, readily available solvent because of its low viscosity and the high solubility for iodine and tin (IV) iodide in benzene. It is convenient to prepare solutions of 10 g of iodine in 100 ml benzene and to obtain weaker solutions by dilution.

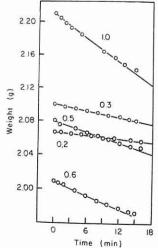


Figure 1. Variation of weight of discs with time when immersed in solutions of different concentrations. Concentrations (g I_2 in 10 ml) marked on lines.

Rate of Loss of Weight of Tin Disc

	0.6 g iodine in 10 ml benzene
Time (min)	Weight (g)
0	2 0091
1	2.0075
2	2.0052
4	1.9985
6	1.9930
8	1.9878
10	1.9830
12	1.9782
14	1.9738
15	1.9716

Readings can be taken at 2 min intervals as soon as the balance is steady. Seven or eight readings are usually taken as is shown in the table, but reasonably accurate rate constants could be obtained in a shorter time. The loss of weight occurs fast enough for the student to see a continuous movement of the scale of the balance. Runs with a succession of iodine solutions of different concentrations yield the plots shown in Figure 1. These can be combined to give the plot in Figure 2. From the latter the students can clearly see that:

Rate of loss of tin = k [I₂].

Thus the nature of first-order behavior can be established. This interpretation of the results can be recognized by students who have not yet learned to integrate.

It may be of interest to note that this experiment originated in a small piece of work undertaken in 1944 by one of the writers, then in his last year at school, and his chemistry master E. J. F. James¹ (now Lord James of Rusholme, Vice-Chancellor of the University of York).

¹ Trotman-Dickenson, A. F. and James, E. J. F., J. Chem. Soc., 736 (1947).

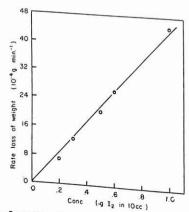


Figure 2. Dependence of rate of loss of weight of tin discs on concentrations of iodine solutions.

THE KINETIC DERIVATION OF THE LAW OF MASS ACTION FOR THIRD-ORDER REACTIONS

J. Weninger and S. Meier

Table 1 displays some kinetic rate laws for various types of reaction that will be found in grammar school chemistry textbooks. In addition to the relationship (1.2) and (2.2) for reactions of type (1.1) and (2.1), rate laws such as (3.2) and (5.2) are often given, from which one can deduce the general relationship (6.2). This is a good thing, since students should be taught to understand reactions of the third order. In our experience they cannot do this if the equations (3.2) and (5.2) are

$[A + B \rightleftarrows C + D]_{c_B = konstant}$	(1.1)	$v_{\rightarrow} = k \cdot c_A$	(1.2)
$A + B \rightleftarrows C + D$	(2.1)	$v_{\rightarrow} = k \cdot c_A \cdot c_B$	(2.2)
	(3.1)	$v_{\rightarrow} = k \cdot (c_A)^2$	(3.2)
$2 \text{ A} \rightleftarrows \text{B} + \text{C}$	(4.1)	$v_{\rightarrow} = k \cdot (c_A)^2 \cdot c_B$	(4.2)
$2 A + B \rightleftarrows C + D$	(5.1)	$v_{\rightarrow} = k \cdot (c_A)^2 \cdot c_B$	(5.2)
2 A + B ≠ 2 C		$v_{\rightarrow} = k \cdot (c_A)^a \cdot (c_B)^b \cdot (c_C)^c \dots$	(6.2)
$aA + bB + cC + \dots \rightleftarrows$ $dD + eE + fF + \dots$	(6.1)		

Table 1. Types of Reaction and the corresponding Kinetic Rate Laws.

only 'deduced' in an unsatisfactory and unconvincing way from equation (2.2) without any clearly recognizable reasons being given - in other words, if they are not explained logically. In none of the high-school words, unfortunately, in which the formation and decomposition of textbooks, unfortunately, in which the formation and water are dealt with sulphur trioxide hydrogen iodide, ammonia and water are dealt with sulphur trioxide hydrogen iodide, reasons why, in equations (3.2), (5.2) are there sufficiently convincing reasons why, in equations

and (6.2), there are one or more concentrations to the second or higher power. This is also true of the frequently used equation

$$\frac{\left(c_{A}^{2}\right)^{2} \cdot c_{B}}{\left(c_{C}^{2}\right)^{2}} = K \tag{5.3}$$

More often than not one finds explanations such as: "When several components of the same kind occur in the equation for the reaction, corresponding (!) powers of the concentration appear in the rate

"When several molecules of the same type are involved in a chemical reaction, it follows (!) that the concentration of the particular substance concerned must be inserted for each molecule separately to obtain the equilibrium equation". Nor is the student helped in university textbooks if he wants to obtain a clear picture of the reasons why the concentrations of substances A and C are entered as squared terms in equation (5.3). Here, too, he finds only generalized and unsatisfactory statements such as: "For a quite general chemical

$$c \cdot C + d \cdot D + e \cdot E \dots \text{ etc.}$$
 $f \cdot F + g \cdot G + h \cdot H \dots \text{ etc.}$ mass action law is

the mass action law is

$$(F)^{f} (G)^{g} (H)^{h} \cdots / (C)^{c} (D)^{d} (E)^{e} = K$$

Accordingly (!) we must raise the concentration of the reacting substances to the power which corresponds to the number of moles involved in the chemical reaction". Even in some physical-chemistry textbooks known to us there are no satisfactory explanations given: "It is easy to see (!) that in the following example nothing of importance changes when molecules A and B become identical so that the condition for dynamic equilibrium for the reaction

$2A$
 $\stackrel{}{\longleftrightarrow}$ A_2 is $(c_A)^2$ / $(c_{A_2}) = K_c$

Such explanations, which can be quoted in great numbers, bypass students' difficulties. They just cannot see how 'it follows' that concentrations must be entered as higher powers in the equations. It does not even occur to most of them that these concentrations should be entered to any other power than one; they have already seen many examples in which the rate of reaction is proportional to the first power of the concentrations.

If the particular reaction is not explained by the teacher straightaway but, instead, they are simply told that the concentrations of those substances of which two or more molecules are involved in collisions do not appear to the first power in the mass law equation, then when they next deal with this problem they arrive at conclusions even further away from the truth. For they argue roughly as follows: since the concentrations of the substances mentioned diminish more rapidly than the others, they occur in the mass law equation with exponents less than unity.

Florke, in his textbook and 'method' goes one step further than the majority of textbooks and shows with appropriate examples how correct results are obtained from the mass action law using exponents greater than 1. Even this method does not provide a sufficient substitute for a logical derivation. If students are to arrive at a proper understanding of the mass action law for reactions of a third or what seems to be a higher order one cannot afford to leave out of account the kinetic relationships in these reactions. The correctness of the exponents can be shown most clearly from kinetics and, in fact, must be explained in this way. This is all the more necessary and urgent since, as yet, there are no third order reactions suitable for experimental examination in schools.

In order to isolate the difficulties of the kinetic derivation a second order reaction (where only a single kind of particle is involved) is studied before dealing with reactions of the type which are the ones usually discussed in the textbooks. A reaction of type (3.1) such as the decomposition of hydrogen iodide, which is discussed in some books, must therefore be examined. If the students cannot find the correct relationship between rate of reaction and the concentration (which will usually be the case) rate of reaction and the concentration as being relevant. But even if they equation (3.2) must then be explained as being relevant. But even if they know the result students do not often find a proper explanation for its derivation 2.

Only in one exceptional case did a mathematically gifted student discover the correct relationship for himself and develop it in front of the class in the correct relationship for himself and develop it in front of the class in roughly the same way as it is shown here.

This must be taken as proof that the relationship is not so easy to understand as one might think from the explanations quoted in textbooks.

After getting used to it and after some practice students soon fall back on the kinetics of reactions with which they are already familiar - ester saponification for example [ref. 1] - to help them understand what happens in reactions of type (2.1). These same lines of thought should also be carefully followed by the students in order to make equation (2.2) clear to them or to help them to derive it for themselves.

The governing factor in a chemical reaction is the collision of particles (molecules or ions). If a vessel of Volume V contains one particle from each of two substances reacting with each other, and if these collide once, on average, in a time t, then when a second particle from one of the substances is introduced into the vessel (and the temperature remains constant) there are, on average, two collisions between one particle of one kind and one of the other during time t. (In total there are three collisions during time t between the three particles). Table 2 shows clearly what happens when more and more particles are introduced into the vessel.

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$A + B \rightarrow C + D$ $v_{\rightarrow} = k \cdot c_A \cdot c_B$	а • •		7 2 3			7 2 3	0 6 6	
$ \begin{array}{c} c \to 1 \\ c \to 2 \\ c \to 3 \end{array} $	n_2	1	$\frac{2}{a \rightarrow 1}$	$ \begin{array}{c} 3 \\ \hline a \rightarrow 1 \\ a \rightarrow 2 \end{array} $	1	$ \begin{array}{c c} 2 \\ \hline 2 \\ \hline a \rightarrow 1 \end{array} $	$ \begin{array}{c} 2 \\ 3 \\ \hline a \rightarrow 1 \\ a \rightarrow 2 \end{array} $	$ \begin{array}{c} 4 \\ a \rightarrow 1 \\ a \rightarrow 2 \\ a \rightarrow 3 \end{array} $	
		1 x 1	1 x 2	1 x 3	b→1	$b \rightarrow 1 \\ b \rightarrow 2$	$b \rightarrow 2$	$b \rightarrow 2$ $b \rightarrow 3$ $b \rightarrow 4$ $c \rightarrow 1$ $c \rightarrow 2$	

Table 2. Number of collisions in unit time between 1 particle of each of the two types for the reaction indicated in the left hand column. One black circle represents one particle of one type per unit volume; one open circle O represents particles per unit volume; z = Z/t = no. of collisions per unit time. (Z = L/t = no) individual black and open circles).

If n_1 is kept constant (columns 1 - 6), z changes in proportion to n_2 :

$$[z = k_1 \cdot n_2]_{n_1 = constant}$$

If n_2 is kept constant (column 2, 5, 3, 6) z changes in proportion to n_1 :

$$[z = k_2 \cdot n_1]_{n_2 = constant}$$

Together this gives

$$z = k_3 \cdot n_1 \cdot n_2$$

The number of collisions of particles of one kind with the other kind in unit time changes according to the number of particles of each of the two kinds per unit volume. Not every collision leads to reaction. At constant temperature, however, the number r of 'elementary reactions' in a given time is proportional to the number of collisions z in the same time:

$$r = k_4 \cdot z$$

And thus

$$r = k_5 \cdot n_1 \cdot n_2$$

The reaction velocity v is given by

$$v = k_6 \cdot r$$

and, therefore,

$$v = k_7 \cdot n_1 \cdot n_2$$

As the number n of one type of particle per unit volume changes according to its concentration c in the homogeneous mixture the following relation (2.2) is finally obtained:

$$_{v} = k. c_{A}. c_{B}$$

 $T_{\rm his}$ can also be obtained by experiment. Working along similar $l_{\rm ines}$ the relationship (3.2) can now be found (Table 3).

$2 A \rightarrow B + C$ $v_{\rightarrow} = k \cdot (c_A)^2$	7002		250	2 5 5 4	
n	2	3	4	5	p
zu einer cönnen	1→2	$ \begin{array}{c} 1 \to 2 \\ 1 \to 3 \end{array} $	$ \begin{array}{c} 1 \rightarrow 2 \\ 1 \rightarrow 3 \\ 1 \rightarrow 4 \end{array} $	$ \begin{array}{c} 1 \rightarrow 2 \\ 1 \rightarrow 3 \\ 1 \rightarrow 4 \\ 1 \rightarrow 5 \end{array} $	
Teilchenstöße, die zu einer Reaktion führen können		2→3	$ \begin{array}{c} 2 \rightarrow 3 \\ 2 \rightarrow 4 \end{array} $	$ \begin{array}{c} 2 \rightarrow 3 \\ 2 \rightarrow 4 \\ 2 \rightarrow 5 \end{array} $	
Teilcher Reakti			3→4	$3 \rightarrow 4 \\ 3 \rightarrow 5$	-
				4→5	
2	1	1+2	1+2+3	1+2+3+4	$1+2+\ldots+(p-2)+(p-1)$

Table 3. Number of collisions in unit time between two particles of the same type. z is shown by the number of lines joining two circles.

The number of collisions in unit time changes in proportion to the sum S of an arithmetic progression of (n-1) terms, the first term being 1 and the last term (n-1). This total is given by

$$S = \frac{n}{2} \cdot (n - 1)$$

(The summation formula for m terms is

$$S_{m} = \frac{m}{2} (m + 1).$$

For m = (n - 1) this becomes

$$S_{(n-1)} = \frac{n-1}{2} [(n-1) + 1] = \frac{n}{2} \cdot (n-1)$$

Thus we can write

$$z = k_8 \cdot \frac{n}{2} \cdot (n - 1)$$

This result does not seem at first sight to lead to the correct relationship (3.2). The way out will soon be seen however. Since there are always

very many particles involved in chemical reaction (the smallest amount of substance that can be weighed at present contains at least 10^{10} particles) n \gg 1, and we can write

$$z = k_9.n^2$$

The number of collisions between particles of the same type in unit time (when, and only when there is a very large number of particles) varies with the square of the number of particles per unit volume. This leads quickly to the desired result (3.2)

$$v = k.(c_A)^2$$

which can really only be understood if derived in this context.

It is now no longer difficult for students to obtain equation (5.2) for reactions of type (5.1).

	I		δ •	g b	a b	
$2 A + B \rightarrow 2 C$, b		9	2 9	
$v_{\rightarrow} = (c_A)^2 \cdot c_B$	1 2		3	2	2	р
n_1	1	2	2	3	4	q
n_2	$\frac{2}{a \to 1 \to 2}$	$\frac{2}{a \to 1 \to 2}$	$a \rightarrow 1 \rightarrow 2$	$ \begin{array}{c} a \to 1 \to 2 \\ a \to 1 \to 3 \end{array} $	$ \begin{array}{c} a \to 1 \to 2 \\ a \to 1 \to 3 \\ a \to 1 \to 4 \end{array} $	
iner			F	$a \rightarrow 2 \rightarrow 3$	$\begin{array}{c} a \rightarrow 2 \rightarrow 3 \\ a \rightarrow 2 \rightarrow 4 \end{array}$	
zu e					$a \rightarrow 3 \rightarrow 4$	
Teilchenstöße, die zu einer Reaktion führen können		$b \rightarrow 1 \rightarrow 2$	$b \rightarrow 1 \rightarrow 2$	$b \rightarrow 1 \rightarrow 2$ $b \rightarrow 1 \rightarrow 3$	$b \rightarrow 1 \rightarrow 2$ $b \rightarrow 1 \rightarrow 3$ $b \rightarrow 1 \rightarrow 4$	
henstö ıktion				$b\rightarrow 2\rightarrow 3$		
eilc Rea			$c \rightarrow 1 \rightarrow 2$		$b \rightarrow 3 \rightarrow 4$	
Г			3×1	2 x (1+2)	$2 \times (1+2+3)$	$p \times (1 + 2 + + [q-1])$
Z	1x1	2 x 1		:+ time	between 2	particles of one kind

Table 4. Number of collisions per unit time between 2 particles of one kind One open circle represents one particle and a single particle of a second kind. One open circle represents one particle in a and a single particle of a second which two particles participate in a per unit volume of the substance from which represents one particle per unit volume of per unit volume of black circle represents in reaction; z is given by single reaction; one black only 1 particle particles and one black one. a substance from which only 1 particle from two open circles and one black one.

When n_2 is constant, z is proportional to n_1

$$z = [k_{10}, n_1]$$
 $n_2 = constant$

when \mathbf{n}_1 is constant the relationship between \mathbf{z} and \mathbf{n}_2 is

[z =
$$k_{11} \cdot \frac{n_2}{2}$$
 ($n_2 - 1$)]

 $n_1 = constant$

For n₂ >> 1,

$$[z = k_{12}.(n_2)^2]_{n_1} = constant$$

This gives

$$z = k_{13}.n_1.(n_2)^2$$

and, finally, equation (5.2)

$$v = k. (c_A)^2. c_B$$

As has been said already, a reaction of this type cannot be examined experimentally in schools. It seems all the more necessary then to go over, in school, a reaction which has been analysed kinetically and about which it can be said with some certainty that it is of the third order. Such a reaction is the formation and decomposition of nitrogen di oxide [ref. 2].

$$^{2}NO + O_{2} \longrightarrow ^{2}NO_{2}$$

This is more suitable for class discussion than one of the (1.1) type reactions which should of course also be discussed for their technical and historical importance. It is important - for the reasons stated above - that the nitrogen dioxide reaction is studied first. Furthermore, it is now possible to test the correctness of the kinetic law derived for this reaction by using experimentally determined rather than theoretical values.

Students enjoy pursuing these lines of thought in other types of reaction. They easily obtain the equation

$$v = k \cdot c_A \cdot c_B \cdot c_C$$

and, after a bit of a struggle,

$$v = k. (c_A)^3$$

For the derivation of this latter equation the correct value of ${\bf z}$ can be found,

and then the approximate value,

$$n \gg 1$$
, $\frac{1}{6}$. n^3 .

References.

- [1] S. Meier, An Experiment to find a rigorous derivation for the Law of Mass Action, Der Mathematische und Naturwissenschaftliche Unterricht, 1962/3, vol. 15, 209.
- [2] J. Eggert, Textbook of Physical Chemistry, 1948, 585.



3. Acids and bases

3. Acides et bases

The heading "Acids and bases" includes a great deal of chemistry. Very elementary courses will include a discussion of acids, although at this level only very simple diagnostic tests are needed—a sour taste, an ability to change the colour of "indicators" or the liberation of carbon dioxide by reaction with carbonates for example. Senior classes will need to know something about the interactions of ions with solvent molecules when the chemistry of reactions in solution is being discussed. This will mean some knowledge of the electronic theory of atomic and molecular structure, and the development of an ability to think in three dimensions. Once this background has been established it becomes relatively easy to provide a framework for an extended discussion of acid-base reactions in which a large number of experimental observations can be correlated.

Most of the reactions of inorganic chemistry so far studied have been carried out in aqueous solution. The papers reproduced in this section show how acid-base definitions for aqueous systems can be extended to cover a wider range of chemical reactions. The paper by H. Spandau discusses and compares the original Arrhenius theory with the later theories of Lowry-Brönsted, Franklin, Lewis et al. The article by G. H. Aylward and J. Zyka which covers the same ground at the same level (senior) has been included deliberately because it shows how the material of the first paper-designed for reading by the student at home or in the class-room—can be presented by the teacher as a lecture with demonstrations. The demonstrations, many of which can be arranged for display using an overhead projector, justify the extension of the Arrhenius acid-base theory to a much wider range of reactions in solution.

The article by R. J. Gillespie shows how measurements of the depression of the freezing point of a solution, so often treated as an isolated topic in physical chemistry courses, can be woven into a treatment of the acid-base concept in non-

Ce titre « Acides et bases » recouvre une partie importante de la chimie. Même les cours très élémentaires comporteront une étude des acides, encore qu'à ce niveau on puisse se contenter d'expériences très simples permettant de reconnaître la présence d'un acide: saveur aigre, action sur les « indicateurs » colorés ou dégagement d'anhydride carbonique par réaction avec les carbonates par exemple. Les étudiants plus avancés devront avoir quelques notions sur l'interaction des ions avec les molécules de solvant au moment où ils étudieront la chimie des réactions en solution. Cela signifie qu'ils devront posséder quelques connaissances sur la théorie électronique de la structure des atomes et des molécules et avoir acquis la capacité de penser en trois dimensions. Une fois ces conditions fondamentales réunies, il devient relativement facile d'établir le cadre d'une étude détaillée des réactions acides-bases permettant de relier ensemble les résultats d'un grand nombre d'observations expérimentales. La plupart des réactions de chimie minérale étudiées jus-

qu'ici ont été effectuées en solution aqueuse. Les articles reproduits dans la présente section montrent que les définitions des acides et des bases valables pour les réactions en système aqueux peuvent être étendues à une plus grande variété de réactions chimiques. L'article de H. Spandau étudie et compare la théorie initiale d'Arrhenius avec les théories plus récentes de Lowry-Brönsted, Franklin, Lewis et autres. L'article de G. H. Aylward et J. Zyka, qui traite de la même question au même niveau (second cycle), a été inclus intentionnellement parce qu'il montre comment la matière du premier article — destinée à être étudiée par l'élève chez lui ou en classe — peut être présentée par le professeur sous la forme d'un cours accompagné de démonstrations. Ces démonstrations, dont un grand nombre peuvent être effectuées sous forme de projections à l'aide d'un rétroprojecteur, justifient l'extension de la théorie d'Arrhenius sur les acides

L'article de R. J. Gillespie montre comment la question de la mesure de l'abaissement du point de congélation d'une solution, si souvent traitée comme un sujet à part dans les cours de chimie physique, peut être rattachée à l'étude de la

et les bases à une bien plus grande variété de réactions en

aqueous systems. The partial ionization of many solvents can often be demonstrated by this technique.

notion d'acidité et de basicité dans les systèmes non aqueux. Cette technique permet souvent de démontrer l'ionisation partielle de nombreux solvants.

MODERN THEORIES OF ACIDS AND BASES

by H. SPANDAU

The Arrhenius theory of acids and bases depended Introduction on water, which in his time was the only solvent used to obtain a reaction involving ions. However, experiments over the last seventy years using non-aqueous ionising solvents such as liquid ammonia, anhydrous liquid hydrogen fluoride, glacial acetic acid or liquid sulphur dioxide - to name but a few - have shown that we can define acids and bases in a more general way. Three modifications of the Arrhenius theory have been proposed:

- 1. The Proton Theory (proposed by Bronsted)
- 2. The Electron Theory (proposed by Lewis) and 3. The Solvent Theory (proposed by Franklin, Jander and others).
- Let us look first at the way in which ideas on acids and bases have developed throughout history. Whereas in 1780 Lavoisier had maintained that oxygen was an essential ingredient of acids and thus named the element 'oxygenium', in 1814 Davy discovered substances with acid properties that did not contain oxygen (e.g. HCl). Davy concluded that there was no one element responsible for acid reactions, and this idea is maintained in two of the modern theories - the Electron Theory and the Solvent Theory. During the last 100 years however research into the nature of acids took another direction. Many chemists concluded, from Davy's observations, that hydrogen was the element responsible for acid behaviour, and this idea is retained in the Arrhenius and the Bronsted theories. Arrhenius (1887) defined acids as compounds which produce positively charged hydrogen ions in aqueous solution, while bases produce negatively nydrogen ions in aqueous solution. In neutralisation reactions, charged hydroxyl ions in aqueous with hydroxyl ions for hydrogen ions of an acid combine with hydroxyl ions from a base to form undissociated water molecules. This still appears in most contemporary textbooks as the equation

Acid + Base = Salt + Water

The Three Modern Theories Let us now turn to the modern theories. Work on a non-aqueous ionising solvent, liquid ammonia, was begun in 1900. In the early nineteen twenties it was seen that phosgene has a similar ionising effect on dissolved electrolytes. Work followed on the solvosystems of anhydrous hydrogen fluoride and liquid sulphur dioxide. More and more ionising solvents have been discovered in the last thirty years.

One basic result of this work was the discovery that a definition of acids and bases was not necessarily linked with water as solvent, but that to some extent in non-aqueous ionising solvents completely different substances may possess acid or base qualities. This meant a complete departure from the Arrhenius theory - a line followed by Lewis in his Electron Theory. Others thought it logical to modify the Arrhenius theory to fit the new facts. Thus there were two approaches:

- 1. The Brønsted approach: he did not introduce the solvent into his definitions, and he retained the proton as the essential principle of acidity;
- 2. The line of enquiry leading to the Solvent Theory. Neither protons nor hydroxyl ions were brought into the definitions, but they were closely linked with the self-dissociation of individual solvents, just as they were linked with the dissociation of water in the Arrhenius theory.

The most comprehensive and therefore the most widely applied of the three modern theories are the Electron and the Solvent theories. The Proton theory, on the other hand, is limited in its application to groups of solvents containing protons such as water, liquid ammonia, liquid hydrogen fluoride, glacial acetic acid, anhydrous nitric and sulphuric acids etc. The theory cannot be applied to ionising solvents not containing protons such as the 'oxidotrope' solvents liquid sulphur dioxide and liquid dinitrogen tetroxide, or to the 'chlorotrope' solvents of phosphorus oxychloride, nitrosyl chloride, as iodine mono- and tri- bromide etc, the bromotrope' systems such bromine trifluoride, iodine pentafluoride, selenium tetrafluoride, arsenious tetrafluoride etc. We will now discuss the Proton Theory.

The Bronsted Theory Bronsted defined an acid as a substance which shows a tendency to and is capable of dissociation with the production of protons. Acids are proton doners and bases proton acceptors that can combine with protons. They can be neutral molecules or even ions, so that we can have cation, anion and neutral acids and similarly with bases.

Tabelle 1 Protonen – Theorie der Säuren und Basen

Anionensäure:	HSO ₄ -		+	SO ₄ ²⁻
Neutralsäure: Kationensäure:	HCl NH₄+	\rightleftharpoons H ⁺	++	Cl- NH ₃

Table 1: Proton Theory of Acids and Bases

All the examples shown in Table 1 illustrate the separation of a proton from an acid to form a base, and that when the reaction is reversed an acid is reformed. Each acid produces a specific base, and Brønsted defined these pairs as a 'corresponding acid-base system'. Acids react, and only then as proton donors, when a proton acceptor is present. Consider the reaction between hydrogen chloride and ammonia:

ide and ammonia.

$$HC1 + NH_3 \rightarrow NH_4^+ + C1^-$$

The proton donor HCl surrenders its proton to the acceptor NH $_3$ Thus NH $_4$, the acid corresponding to NH $_3$, and Cl, thebase corresponding to HCl are formed. As a generalisation - reaction between an acid and a base proceeds according to a 'doubly-corresponding acid-base system':

This is the basic equation of the $\mathrm{Br}\phi$ nsted theory. It covers not only all neutralisation reactions but also solvolysis in prototropic solvents and ionisation of 'ansolvo' acids and bases as the examples given below in Tables 2 and 3 show.

The equations for 'solvoneutralisations' in water, ammonia, liquid hydrogen sulphide and glacial acetic acid in Table 2 clearly show the amphoteric nature of these ionising solvents, for the

undissociated molecules of the solvent act both as acid 2 and base 1 Thus water is the acid corresponding to the base OH and also the base corresponding to the acid H₃O . In other words it acts as a proton donor or proton acceptor according to the nature of its partner, and the same thing is true for the molecules of the other ionising solvents.

Table 2. Neutralisation and Solvolysis Reactions in Prototropic Solvents.

 ${\it Tabelle~2}$ Neutralisations-Reaktionen in prototropen Lösungsmitteln

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9	
KCN in H_2O : H_2O + $CN^ \rightleftharpoons$ HCN NH_4Cl in H_2O : NH_4^+ + H_2O \rightleftharpoons H_3O $Cd(CH_3COO)_2$ in H_3S : H_3S + SO_4^{2-} \rightleftharpoons H_2SO	₂ O + H ₃ + S +	Base 1 H ₂ O NH ₃ H ₂ S CH ₃ COOH
KCN in H_2O : H_2O + CN- \rightleftharpoons HCN NH ₄ Cl in H_2O : NH_4^+ + H_2O \rightleftharpoons H ₃ O Cd(CH ₃ COO) ₂ in H_2S : H_2S + H_2S	36	
	3O+ 2SO ₄ +	OH- NH ₃ 2 CN- HS-

Table 3. Ionisation of 'Ansolvo' Acids and Bases

Tabelle 3 Ionisation von Ansolvosäuren und Ansolvobasen

Solvolysis reactions, which correspond to hydrolysis in water solution, can be similarly depicted as a 'doubly corresponding acid-base system' (see Table 2). In the hydrolysis of potassium cyanide, water acts as a proton donor with respect to the proton acceptor CN forming an acid HCN and a base OH . In the hydrolysis of ammonium chloride, NH₄ acts as the proton donor and H₂O as the proton acceptor, forming the base NH₃ and the acid H₃O + . Solvolysis in the non-aqueous solvents HCN and H₂S shown in Table 2 can be explained in a similar way and the corresponding equations formulated. When solvolysing cadmium acetate in H₂S the CH₃COO ion acts as the proton acceptor towards H₂S as the proton donor. Proton transfer produces undissociated acetic acid and HS ions.

Table 3 gives a few examples of the ionisations that occur when ansolvo acids and bases dissolve in water and some non-aqueous solvents (prototropic). Here again we get the same reaction involving the 'doubly corresponding acid-base system', that is to say protons are transferred from acid 1 to base 2. When ansolvo acids such as HCl are dissolved the solvent molecule acts as a base; when, on the other hand ansolvo bases such as ammonia and the amines are dissolved the solvent acts as an acid. For example, when HCl is dissolved in water, or liquid ammonia, or in liquid hydrogen sulphide, proton transfer to the solvent molecules occurs and acids corresponding to the specific solvents, namely H₃O, NH₄ or H₃S are formed. On the other hand, when the ansolvo base NH₄ is dissolved in water, H₂O is the proton donor and the acid NH₄ and the base OH are formed.

The Proton Theory has the following advantages over the Arrhenius Theory. Brønsted has broadened the basis upon which substances Theory. Brønsted has broadened the bases, but most important of can be classified either as acids or bases, but most important of can be classified either as acids or bases, but most important of can be classified either as acids or bases, for classifying bases all he has considerably widenened the scope for classifying bases all he has considerably widenened the hydroxyl ion as a fundamental by rejecting the special place of the hydroxyl ion as a fundamental component of a base. Furthermore, he has defined the typical component of a base. Furthermore, he has defined the typical component of acids and bases, i.e. neutralisation, solvolysis and reactions of acids and bases, i.e. neutralisation, solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation, solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neutralisation for the solvolysis and reactions of acids and bases, i.e. neu

The Solvent Theory Let us now consider the basic principles of the Solvent Theory, which has been developed by Franklin, Cady and Jander among others. They define acids and bases without referring to the ions of water - protons and hydroxyl ions. They firmly link their definitions to the self-dissociation properties of specific solvents. Here the fundamental idea of the Arrhenius theory for wateras solvent is transferred to any ionising solvent. Acids in a particular solvent are defined as those substances which when dissolved in this solvent increase the concentration of the cations of the solvent. It follows that bases in a particular solvent are substances which when dissolved in the solvent increase the concentration of the anions of the solvent.

Table 4 shows the dissociation of some ionising solvents and the types of substances formed with their acid or base functions. To prevent confusion with the acids and bases of the Arrhenius theory it is better to speak of solvo-acids and solvo-bases, especially in systems such as liquid ammonia (ammono-acids and bases), or liquid sulphur dioxide (sulphito-acids and bases). The first four examples in Table 4 show that with prototropic solvents the cations from the solvent are solvated protons such as the NH₄ ions in liquid ammonia. Following this rule, all ammonium compounds act as acids in liquid ammonia. The anion of the solvent in liquid ammonia is the NH₂ ion, so that amides act as bases in liquid ammonia. The CN ion is a solvobase in liquid HCN and HS a solvobase in liquid $\mathrm{H}_{2}\mathrm{S}$. The second group of Table 4 includes oxidotropic and chlorotropic solvents. The dissociation of liquid sulphur dioxide produces SO₂ cations and SO₃ anions, so that thionyl compounds act as solvoacids and sulphites as solvobases in this solvent. When liquid dinitrogen tetroxide dissociates NO cations and NO anions are formed, so that the nitrosyl compounds are solvoacids and nitrate ions solvobases in this solvent. Chlorotropic solvents produce Cl ions assolvent anions, so that in these systems chlorides

In the Solvent Theory, therefore, whether a compound functions as an acid or a base is determined by the way in which the solvent dissociates. This results in a particular substance having different functions in different solvents. Thus, as is well known, NH Cl is a salt in the water solvosystem, whereas in liquid ammonia it belongs, as do all other ammonium ion compounds to the ammonoacids. The salt of an aquo-system, KNO , becomes the solvo base in N₂O₄. The compound NOSbCl acts as an acid in the solvents NOCl and N₂O₄, whereas it is a solvosalt in liquid SO since the ions it releases are not the same as those produced by dissociation of the solvent.

Table 4: Solvoacids and solvobases

Tabelle 4
Solvosäuren und Solvobasen

Solvens	E	ligen	dissoziatio	n		Solvosäuren	Solvobasen		
H ₂ O HCN H ₂ S	2 H ₂ O 2 HCN 2 H ₂ S	1 1	H ₃ O+ H ₂ CN+ H ₃ S+	+++++	OH- CN- SH-	Arrhenius-Säuren Arrhenius-Säuren Arrhenius-Säuren	Hydroxide Cyanide Hydrogensulfide		
NH ₃ SO ₂	2 NH_3 2 SO_2	#	NH ₃ + SO ²⁺	+	NH ₂ - SO ₂ -	Ammonium-Verb. Thionyl-Verb.	Amide Sulfite		
N₂O₄ NOCl	N ₂ O ₄ NOCl	≥	NO+ NO+	+	NO ₃ -	Nitrosyl-Verb. Nitrosyl-Verb.	Nitrate Chloride		
SOCl ₂ SeOCl ₂	SOCl ₂ SeOCl ₂	;	SOCl ⁺ SeOCl ⁺	++	Cl-	Chlorothionyl-Verb. Chloroselenyl-Verb.	Chloride Chloride		

Table 5: Solvo-neutralization

Tabelle 5
Solvoneutralisationen

Solvens	Solvosäure	+	Solvobase	=	Solvesalz	+	Solvens	
	H ₃ O+Cl-	+	K+OH-		K+Cl-	+	2 H ₂ O	
H_2O	NH ₄ +Br-	+-	$K+NH_2-$	==	K+Br-	+	2 NH	
NH_3	H ₃ S+Cl-	+	Na+SH-	====	Na+Cl-	4	2 H _o S	
H_2S	SO ²⁺ (SCN ⁻) ₂	+	K+2SO32-	=	2 K+SCN-	+	2 SO.	
SO ₂	NO+Cl-	+	Ag+NO ₃ -	==:	Ag+Cl-	4-	N_2O_4	
N_2O_4	NO+[SbCl ₆]-	1	(CH ₃) ₄ N+Cl-	=	(CH ₃) ₄ N[SbCl ₆]	+	NOCI	
NOCl	SOCI+[AlCl ₄]	+	(C2H5)4N+Cl-	=	$(C_2H_5)_4N[AlCl_4]$	+	SOCI ₂	
SOCl ₂	I+Cl-	+	K+J-	=	K+Cl-	+	J_2	

Table 6: Reactions of solvolysis

Tabelle 6 Solvolyse-Reaktionen

1072.167	Solvosalz	+	Solvens	=	Solvobase	+	Solvosäure
Solvens	501003412		H ₂ O		КОН	+	HCN
H ₂ O	KCN	+	H ₂ S	=	CdS	+	2 CH₃COOH
H ₂ S	Cd(CH ₃ COO) ₂	I	2 HCN	===	2 AgCN	+	H_2SO_4
HCN	Ag_2SO_4	1	2 HNO₃	=	$Cd(NO_3)_2$	+	2 CH ₃ COOH
HNO ₃	$Cd(CH_3COO)_2$	1	6 NH ₃	=	Ge(NH) ₂	+	4 NH₄Cl
NH ₃	CeCl.	1	$2 SO_2$	=	K_2SO_3	+	SO(CH ₃ COO) ₂
SO_2	2 KCH ₃ COO	T	$2 N_2 O_4$	=	$Zn(NO_3)_2$	+	2 NOCl
N_2O_4	ZnCl ₂ NaCN	1	J_2	=	NaJ	+	J(CN)

We must now consider the following points: what reasons are given for these solvent theory definitions of acids and bases?; are the definitions logical and can they be substantiated? Many observations show that solvoacids and solvobases defined in this way do behave in the particular solvent in exactly the same way as the Arrhenius acids and bases do in water. This similarity in chemical behaviour is shown above all in neutralisation and solvolysis, two types of reaction dependent upon the characteristic properties of acids and bases.

Table 5 gives some examples of neutralisation reactions in various solvosystems. The reactions are analogous to those in water between acids and bases producing salt and water. Reaction between a solvoacid and a solvobase produces a solvosalt and solvent molecules. In water solution, the protons of the dissolved acid, the cation of the solvent, cobine with hydroxyl ions of the base, that is with anions of water, to form undissociated water molecules. In tye same way in solvoneutralisation, the cation of the solvoacid, which is the cation of the solvent, reacts with the anion of the solvobase, the anion of the solvent, to form undissociated solvent molecules. For example, in liquid dinitrogen tetroxide, the NO ion of the solvoacid NOCl combines with the NO $_3$ ion of the solvobase AgNO $_3$ to form undissociated N $_2{\rm O}_4$. Such solvoneutralisations have been tested and confirmed in various ways, as, for example, by extracting the product of the reaction - the solvosalt - and analysing it. Furthermore, in many solvosystms the acid-base indicators used in aqueous systems can also be used because, as with water, they change colour as the solutions changes from a solvoacid to a solvobase. The solvoneutralisation can also be followed and clarified by means of conductometric and potentiometric titrations.

Table 6 gives some examples of Solvolysis reactions in various ionising solvents. These correspond exactly to hydrolyses in aqueous solution. Thus certain solvosalts react with solvent molecules on solution, or with their ions, to form solvoacids or solvobases. For example, in liquid SO_2 , soluble acetates decompose solvolytically to form sulphite and the and the solvoacid $SO(CH_3COO)_2$, and in $Zn(NO_3)_2$ and the solvoacid NOC1.

It is well known that numerous amphoteric compounds exist in water solution - metal hydroxides which act as acids or bases according as the partner in the reaction is an acid or a strong base.

Such amphoteric compounds exist, and act in the same way, in non-aqueous ionising solvents. Table 7 gives some selected examples. In liquid ammonia, fro example, zinc amide is amphoteric, for it acts as an ammonobase toward the ammonoacid NH $_4$ Cl giving ZnCl $_2$ and NH $_3$. On the other hand it behaves as as ammonoacid toward the strong ammonobase KNH $_2$, forming ammonium zincate K $_2$ (Zn(NH $_2$) $_4$). Zinc nitrate is amphoteric in liquid N $_2$ O $_4$ as can be seen from the equations in Table 7. Zn(NO $_3$) $_2$ acts as a solvobase toward the solvoacid NOCl, but as a solvoacid toward the strong solvobase (R $_4$ N)NO $_3$. In the latter case the nitrato-complex (R $_4$ N) $_2$ Zn(NO $_3$) $_4$ is formed. Finally, as further proof for the definitions of the Solvent Theory

Finally, as further proof for the definitions of the Solvent Theory we might point to the similar behaviour of acids and solvoacids with base metals, and of aquobases and solvobases upon amphoteric metals.

Table 8 gives some examples of this.

Table 7. Amphoteric Compounds and Reactions

Tabelle 7

Table 8. Reactions of Solvoacids and bases with Metals

Tabelle 8

Reaktion von Solvosäuren mit unedlen Metallen

```
\begin{array}{lll} \text{in $H_2O$:} & Zn+2 \text{ HCl} & = ZnCl_2 + H_2 \uparrow \\ \text{in $NH_3$:} & Ca+2 \text{ NH}_4\text{Cl} & = CaCl_2 + 2 \text{ NH}_3 + H_2 \uparrow \\ \text{in $N_2O_4$:} & Zn+2 \text{ NOCl} & = ZnCl_2 + 2 \text{ NO} \uparrow \\ \\ & & \text{Reaktion von Solvobasen mit amphoteren Metallen} \\ \text{in $H_2O$:} & Zn+2 \text{ KOH} & + 2 \text{ H}_2O = K_2[Zn(OH)_4] + H_2 \uparrow \\ \text{in $NH_3$:} & Zn+2 \text{ KNH}_2 & + 2 \text{ NH}_3 = K_2[Zn(NH_2)_4] + H_2 \uparrow \\ \text{in $SO_2$:} & Sn+2 (R_4N)_2SO_3 + 3 SO_2 = (R_4N)_2[Sn(SO_3)_3] \\ R = C_2H_5 & + (R_4N)_2S_2O_3 \end{array}
```

In dilute aqueous solution acids liberate hydrogen from base metals such as zinc. This means that metal ions go into solution whereas the acid cations of the solvent are discharged. Calcium reacts in the same way towards ammonoacids in liquid ammonia solution. Here too the 'acid' NH4 ion is discharged to form an NH4 radical which breaks down into ammonia and hydrogen. behaviour of zinc towards the solvoacid NOTl in liquid N $_2$ O $_4$ solution is similar; the zinc discharges the nitrosyl cation of the solvoacid to form NO which escapes as a gas. The lower half of Table 8 shows reactions of solvobases with amphoteric metals. It is known that zinc dissolves in sgrong aquobases to form hydrozincate and hydrogen. Zinc behaves in the same way in liquid ammonia toward strong ammonobases such as KNH, Ammono-zincate is formed and hydrogen escapes. The last example in Table 8, with liquid SO2 as solvent seems, at first sight, not to fit into the picture. It is true that tin dissolves as sulphitostannate, but the liberation of gaseous SO, formed from the discharge of the cation of the solvent, SO2+, is missing. We might expect sulphur monoxide to be formed. However it is not stable, but rearranges to form sulphur dioxide and sulphur. This latter dissolves in the presence of excess sulphite to form thiosulphate, a reaction which is well known when water is the solvent.

The Solvent Theory has a great advantage over the Proton Theory in that acids are defined much more comprehensively, and they are not restricted to acting as proton donors. The solvent theory, therefore, can be used with all ionising solvents.

The Electron Theory Finally, let us discuss the third of the modern acid-base theories, the Electron Theory. This is based on the work of Lewis, Sidgwick, Luder and others. In this theory acids are defined as acceptors of electron pairs, and bases as donors of electron pairs. The main characteristic of all neutralisation reactions is the formation of a coordinate bond between the acid and base concerned. Bases, or electron-pair donors, are molecules or ions which possess one or more pairs of electrons which are therefore capable of acting as donors in a coordinate bond, therefore capable of acting as donors in a coordinate bond, that is of combining with molecules or ions which have an incomplete electron shell. Acids are substances with incomplete electron shells which can accept electron pairs.

This theory also means a broadening of the standard Arrhenius theory. Acids and bases defined on the Electron Theory form only one special part of the acids and bases of the Arrhenius definition. The characteristic feature of an acid on the Arrhenius theory, the proton, can accept an electron pair, and the hydroxyl theory, the proton can accept an electron pair, and the hydroxyl ion, which characterises the Arrhenius base, has three electron pairs and can therefore act as an electron-pair donor. Acids pairs and can therefore act as an electron are also included and bases as defined by the Brønsted Theory are also included as a special group in the Electron Theory. All Brønsted bases are proton acceptors and consequently donors of electron-pairs. are proton acceptors and the solvobases of the Solvent Theory Finally, the solvoacids and the solvobases of the Solvent Theory also are covered by the Electron Theory.

The formation of a coordinate bond between electron pair donors and acceptors is seen as the main feature of neutralisation deactions. This is also, of course, the case in neutralisation in aqueous solutions

$$H^+ + : \overset{..}{\circ} : H^- \rightarrow H : \overset{..}{\circ} : H$$

In the formation of water a new coordinate bond is made since the proton from the acid with an incomplete electron shell attaches

itself to an individual electron-pair on the oxygen atom of the hydroxyl ion. Let us consider as an example of neutralisation in a non-aqueous ionising solvent reaction in nitrosyl chloride - a non-prototropic solvent. In all neutralisation reactions in this solvent the NO+ ions of the solvoacid combine with the chloride ions of the solvobase to form undissociated nitrosyl chloride. The chloride ions have four lone-pair electrons and act as electron-pair donors toward the NO ions which have incomplete electron shells.

$$: \overset{\cdot}{O} :: \overset{\cdot}{N^{+}} \ + \ : \overset{\cdot}{Cl} : \overset{\cdot}{-} \rightarrow \ : \overset{\cdot}{O} :: \overset{\cdot}{N} : \overset{\cdot}{Cl} :$$

Thus the acids and bases of the Arrhenius theory and the Brøn sted theory as well as the solvoacids and solvobases of the Solvent theory are all acids and bases on the Electron theory. The electron theory goes further however.

Tabelle 9

Elektronenpaar- Akzeptoren	Elektronenpaar- Donatoren
H+	OH-
Ansolvosäuren Lewis-Säuren Cl Cl : B	Ansolvobasen Lewis-Basen H :: N: H : H
BF_3 ; $AlCl_3$; $FeCl_3$; $SnCl_4$; SbF_5 ; $SbCl_5$; SO_3 ; CO_2	$\begin{array}{c} (\mathrm{C_2H_5)_3N};\ \mathrm{C_5H_5N};\\ \mathrm{H_2O};\ \mathrm{C_2H_5OH};\\ (\mathrm{C_2H_5)_2O};\ (\mathrm{CH_3)_2CO} \end{array}$

Table 9 gives a few examples of this extension of the acid-base concept. Molecules such as BCl₃, BF₃, AlCl₃, FeCl₃, SnCl₄, SbF₅, etc., are also compounds with incomplete electron shells and are thus electron-pair acceptors. They are called 'ansolvo'-acids or 'Lewis' acids to differentiate them from the acids of Arrhenius, Brønsted and the solvoacids. In the same way the following compounds are called 'ansolvo'-bases or 'Lewis' bases: NH₃, (C₂H₅)₃N, C₅H₅N,

C₂H₅OH, (C₂H₅)₂O, and (CH₃)₂CO. Each of them contains a lone-pair of electrons on the nitrogen or oxygen atoms. Lewis acids and bases can form coordinate bonds with each other so that the following reaction is a neutralisation on the Electron theory:-

Again the question arises if this extension of the idea of neutralisation is reasonable. The answer is yes. The reaction between boron trichloride and ammonia can be carried out in a neutral organic solvent which does not belong to the group of ionising solvents. Thus a titration can be carried out in chlorobenzene using crystal violet as an indicator. This indicator is violet in basic solutions and yellow in acid solutions, whether the solvent is water or chlorobenzene.

Summary It is difficult to answer the question as to which of the three modern theories is preferable. Each of them has proved useful in special fields and has been shown to be better than the others in that particular sohere. For example, all chemists engaged on research into reactions in ionising solvents use the Solvent Theory, whereas organic chemists, when they are conducting their experiments in neutral organic solvents base their work on the Electron Theory.

ACID-BASE REACTIONS IN AQUEOUS AND NON-AQUEOUS MEDIA

by

G.H. Aylward and J.Zyka

(An article adapted from a lecture and demonstrations presented at the UNESCO Pilot Project on Chemistry in Bangkok.)

Early in the development of chemistry chemists were looking for classifications of substances on the basis of their reactions. The acids were among the first substances identified as a group because of their easily distinguishable properties. Lavoisier was one of the first to recognise the acids in examining the products of combustion of elements. He was led to believe that it was the presence of oxygen in non-metal oxides that gave rise to the acidic character of their solutions. This theory was strongly supported by Berzelius and it was only after Davy had experimented with chlorine and hydrogen chloride that chemists began to accept the theory that the distinctive properties of acids were associated with hydrogen rather than oxygen.

The first comprehensive theory of acids and bases was proposed by Arrhenius towards the end of the 19th Century. Acids and bases were defined as follows: an acid is a substance which dissociates in water to produce hydrogen ions; a base in water produces hydroxyl ions. The success of the Arrhenius acid-base theory resulted from its quantitative interpretation of the strength of acids and bases. This was explained in was manifested by the extent of its ionisation measured by the electrolytic conductance of its aqueous solution.

According to this "water theory" acidity phenomena were quite simple. The strength of acids and bases were accounted for by their respective dissociation constants, $\rm K_a$ and $\rm K_b$:

This is a slight modification of Arrhenius' original definition of a base.

for an acid
$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$
for a base $BOH \rightleftharpoons B^+ + OH^-$

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

The theory recognised that water also ionised to a small extent and, from conductivity measurements in pure water, the extent of the dissociation of water was measured. It was expressed as an ionic product i.e.

$$H_2O \rightleftharpoons H^+ + OH^ K_W = [H^+][OH^-] = 1 \times 10^{-14} \text{ at } 25^{\circ}C.$$

Thus it was recognised that in an aqueous solution the product of the hydrogen ion concentration and the hydroxyl ion concentration remains constant.

The most obvious limitation of the Arrhenius Theory is the narrowness of its application. But we should not overlook the fact that the fundamental ideas are applicable to some other solvents. The theory as it was developed recognised the importance of the self-ionisation of the solvent. The acid properties are dependent on the concentration of the hydrogen ions; the basic properties dependent on the concentration of the other ion of the solvent, the hydroxyl ion.

Comparison of Acid Strength in Water and Anhydrous Acetic Acid.

Let us now look at a comparison between the strength of some acids in aqueous solution and in anhydrous acetic acid. As a visual measure of the aqueous solution and in anhydrous acetic acid. As a visual measure of the acids in water we will use the colour changes of universal strength of the acids in water we will use the colour changes of universal indicator. Universal indicator consists of a mixture of indicators. The indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators are so chosen that the mixture takes up a different colour at indicators.

The acids to be tested are perchloric acid, sulphuric acid, and nitric acid. First two drops of the indicator are added to samples of the concentrated acid. The nitric acid reacts with the indicator solution giving brown fumes

and leaving an amber coloured solution. The sulphuric acid chars the organic dye stuffs that make up the indicator. The perchloric acid gives a deep red colour to the indicator. One conclusion we can draw from this experiment is that these concentrated acids have quite distinctive chemical properties, little in common with one another. Their physical properties are different also. We explain the properties of the first two as those of the covalent compounds HNO_3 and H_2SO_4 . Perchloric acid is probably more highly ionised in the presence of the 25% water which is present in this sample of the acid.

Now we can make up aqueous solutions of these acids of concentrations $10^{-1}\mathrm{M}$, $10^{-2}\mathrm{M}$, $10^{-3}\mathrm{M}$. First the perchloric acid. We see the gradation in colour change of the universal indicator from red-pink to orange. The indicator colours in the dilute solutions of the nitric and sulphuric acid are identical to the colours in perchloric acid - $10^{-1}\mathrm{M}$ pink-red, $10^{-2}\mathrm{M}$ red, $10^{-3}\mathrm{M}$ orange.

The main point arising from this demonstration is the similarity of the acid strengths of these dilute acids in aqueous solution. Although the very concentrated acids are quite distinctive their acid properties are the same in dilute aqueous solution.

The dilute solutions of the acids in anhydrous acetic acid have been prepared as follows. A volume of the concentrated acid sufficient to make a final solution of 10-1M is diluted to 50% of the final volume with glacial acetic acid. Then acetic anhydride is added very slowly stirring constantly with a thermometer until a fresh addition gives no temperature rise. By careful manipulation the solution can be made up to the final volume with anhydrous acetic acid. In this way anhydrous acetic acid solutions of approximately 0.1M perchloric acid, sulphuric acid and nitric acid have been prepared. To each of these solutions we add a small cryst al of the indicator

If we were to use a more sensitive method of measuring hydrogen ion concentrations we would find that in the sulphuric acid the hydrogen ion concentration would be slightly higher than the others due to the contribution of hydrogen ions from the dissociation of the second hydrogen of sulphuric acid.

Malachite green. We see that the perchloric acid solution gives a yellow colour to the indicator, the sulphuric acid solution a yellow-green and the nitric acid a green colour. From the differences in colour of the indicator we conclude that 0.1M solutions of these acids in anhydrous acetic acid have different hydrogen ion concentrations.

If we compare the conductivities of anhydrous acetic acid and water at 25° C we see they are close to one another, 5.5×10^{-8} ohm⁻¹cm⁻¹ for water, 5×10^{-9} ohm⁻¹cm⁻¹ for acetic acid. This indicates that self ionisation takes place in acetic acid also. The self ionisation constant has been reported as 4×10^{-15} i.e. for the dissociation reaction:

$$CH_3COOH \iff H^+ + CH_3COO^ [H^+][CH_3COO^-] = 4 \times 10^{-15}$$

Now if we adapt the Arrhenius water theory to acetic acid we would say that the strength of the acid is related to the concentration of hydrogen ions in acetic acid arising from a given concentration of the particular acid under consideration. If the base in water is the hydroxyl ion, then in acetic acid the base should be the acetate ion - the anion formed as a result of the dissociation of the solvent. The strength of a base in acetic acid will be measured by the concentration of acetate ions arising from a given concentration of the particular base. A base then will be a substance that in acetic acid produces acetate ions.

Our demonstration shows that the same concentrations of perchloric, sulphuric and nitric acids are of different strengths in acetic acid, but to find which is the strongest acid we must know the indicator colours at different hydrogen ion concentrations in acetic acid. We could find which is the strongest acid by measuring the hydrogen ion concentration with the special electrode systems (e.g. the chloranil electrode) developed so that the potential of the electrode responds linearly to hydrogen ion concentration But let us try to do it visually with the Malachite indicator. We accept the hydroxyl ion as the strongest base available in aqueous solution and it is equally well established that the acetate ion is the strongest base available in acetic acid. So let us add anhydrous sodium acetate to each available in accide acid. We see that there is no change in the colour of the indicator in nitric acid, and this colour matches the colour of the indicator in a solution of sodium acetate in acetic acid. colour in the sulphuric acid solution changes to the green colour of the On adding small amounts of sodium acetate to the perchloric nitric acid. On adding passes through the yellow-green colour exhibited acid, the indicator colour passes through the pitric acid in sulphuric acid to the green colour in the nitric acid.

Our interpretation of these colour changes then is as follows: the perchloric is the strongest of the three acids. The nitric acid is so weak perchloric is the strongest colour to the indicator we used. The sulphuric that it does not give an acid colour to the indicator we used.

is intermediate in strength. Acetate ions neutralise acids in acetic acid just as hydroxyl ions neutralise acids in water.

$$H^+ + OH^- \longleftrightarrow H_2O$$
 $H^+ + CH_3COO^- \longleftrightarrow CH_3COOH.$

However, if we test the conductivities of a 0.1M solution of perchloric acid in water and in acetic acid we find a big difference. The water solution of the acid is a good conductor, the acetic acid solution of perchloric acid is a poor conductor. But the conductivities of the pure solvents are not so different - a tenfold difference, in 5×10^{-8} compared to 5×10^{-9} ohm⁻¹. The extent of the dissociation of perchloric acid into ions in these solvents must be vastly different then. We would expect to find an explanation of this difference in the intrinsic properties of the two solvents.

A major difference in the physical properties of these two solvents is found in the magnitude of their dielectric constants. The dielectric constant is a measure of the insulating property of the solvent. Coulomb's law sets down an expression which relates the force acting between two charged particles, \mathbf{e}_1 and \mathbf{e}_2 , to the distance, \mathbf{r} , separating the particles, and the dielectric constant of the medium, \mathbf{D} ,

$$F = \frac{e_1 e_2}{Dr^2}$$

If D is large the force F will be small. D is assigned the value of one for a vacuum. The dielectric constant of water is 78.5, the value for acetic acid is 6.1. Acetic acid has poor insulating properties and the dissociation of ionic substances in acetic acid takes place to only a small extent. The solubilities of ionic salts in acetic acid are much lower than and ammonium chloride are less than 1% in acetic acid but more than 30% in water. Acids also are dissociated to a small extent only in acetic acid. Perchloric acid, which is one of the strongest acids in acetic acid, dissociates to the extent of one molecule in about one million and this is indicated by to a large extent in acetic acid but the ions are immobilised probably by the formation of oppositely charged ion pairs.

We can understand the differences between the strengths of acids in different self-ionising solvents in terms of the extent of their ionisation and dissociation in the solvent. There is no difference in the strengths of

dilute solutions of perchloric acid, sulphuric acid, nitric acid, hydrochloric acid, hydrobromic acid, the hydriodic acid in water because the high affinity of water for the proton, its strong polar property and its high dielectric constant lead to the complete ionisation and dissociation of these acids in water to hydrated hydrogen ions and hydrated anions. The acid strength of these solutions depends on the strength of the hydrated hydrogen ion, and these acids are said to be levelled to the same strength in aqueous solution. In acetic acid solvent these acids are not levelled to the same strength because the affinity of the solvent for the proton of the solute acid is much less and the extent of the ionisation and dissociation is also much less. This gives rise to the differentiation in the strengths of these acids in acetic acid. The order of acid strength is

$$\mathrm{HClO_4}$$
 > HBr > $\mathrm{H_2SO_4}$ > HCl > $\mathrm{HNO_3}$.

In describing acid reactions in various solvents it is important to appreciate the role of the solvent in determining acid strength and to emphasise this point it is convenient and sometimes necessary to show the proton associated with the solvent. One way of doing this is to represent the hydrogen ion in a particular solvent as a proton solvated with one molecule of the solvent. For example, the hydrogen ion in water is molecule of the solvent. For example, the hydronium or hydroxonium represented as H_3O^+ . This ion is called the hydronium or hydroxonium ion. The hydrogen ion in acetic acid is represented as $CH_3COOH_2^+$ or as $CH_3C(OH)_2^+$, this ion is known as the acetic acidonium ion. The first $CH_3C(OH)_2^+$, this ion is known as the acetic acidonium ton. The first solvate is chosen because it is a simple way of showing the interaction of solvate is chosen because it is a simple way of showing the interaction of the proton with the solvent. Self-ionisation reactions of these solvents showing the solvated proton are usually written as follows:

for water
$$2H_2O \longleftrightarrow H_3O^+ + OH^-$$

for acetic acid $2CH_3COOH \longleftrightarrow CH_3C(OH)_2^+ + CH_3COO^-$

This formula is not meant to represent the unique structure of the proton this formula is not meant to represent the unique structure of the proton species has been verified in solid in water. Although the existence of H_3O^+ species has been verified in solid in water. Although the existence of hydrates have been distinguished in perchloric acid monohydrate, a number of hydrates have been distinguished in perchloric acid monohydrate, a number of hydrates have been distinguished in dilute aqueous solutions of strong acids. As well as H_3O^+ these include $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$.

Just as the levelling effect of the solvent on acids depends on the relative acid strength of the solvated proton so the strength of a base in a self-ionising solvent depends on the relative basic strength of the solvent anion. When sodium ethoxide is added to water it reacts with the water forming hydroxyl ions and ethanol:

$$\text{NaOC}_2\text{H}_5 + \text{H}_2\text{O} \longrightarrow \text{Na}^+ + \text{OH}^- + \text{C}_2\text{H}_5\text{OH}.$$

Similar reactions occur with sodium amide and sodium hydride:

In each case these reactions are practically complete. The basic strengths of these solutes in water are the same; they depend on the basic strength of the hydroxyl ion. The solute bases have been levelled to the strength of the solvent base.

In acetic acid solvent the strongest base is the acetate ion and this is not a very strong base. All bases that are stronger than hydroxyl ions in aqueous solution react with acetic acid to produce acetate ions. Sodium hydroxide reacts this way

NaOH +
$$CH_3COOH \longrightarrow Na^+ + CH_3COO^- + H_2O$$
.

Bases such as ammonia, aniline, guanidine and pyridine are all levelled to the same basic strength in acetic acid although they differ markedly in strength in aqueous solution.

Let us turn now to look briefly at two other self-ionising solvents, anhydrous sulphuric acid and liquid ammonia.

Sulphuric acid is a very powerful solvent with a high self-ionisation constant (2 \times 10⁻⁴) and a high dielectric constant (D = 100):

$$^{2\text{H}}_2\text{SO}_4 \iff \text{H}_3\text{SO}_4^+ + \text{HSO}_4^-$$
.

The solvated proton in sulphuric acid solvent is known as the sulphuric acidonium ion. Only a few exceedingly strong acids are capable of donating protons to sulphuric acid. A 0.1 molar solution of disulphuric acid in anhydrous sulphuric acid is dissociated to about 30 per cent:

$$\text{H}_2\text{S}_2\text{O}_7$$
 + H_2SO_4 \Longrightarrow H_3SO_4^+ + HS_2O_7^-

Boric acid, which a weak acid in water, reacts with disulphuric acid to give a strong acid in anhydrous sulphuric acid:

$$H_3BO_3 + 2H_2S_2O_7 \longrightarrow H_3SO_4^+ + B(HSO_4)_4^- + H_2SO_4^-$$

The acid formed would be HB(HSO₄)₄, tetrahydrogensulphatoboric acid. The strongest base is the hydrogen sulphate ion. Metal hydrogen sulphates are strong bases, analogous to alkalies in water. Most other salts and bases are stronger bases than the hydrogen sulphate ion so they react completely with sulphuric acid being levelled to the strength of the solvent base. Sodium chloride decomposes the solvent to form hydrogen sulphate ions:

$$NaCl + H_2SO_4 \longrightarrow Na^+ + HSO_4^- + HCl.$$

Compare this reaction to that of sodium amide with water:

$$NaNH_2 + H_2O \longrightarrow Na^+ + OH^- + NH_3.$$

Acids which are strong in aqueous solution react differently in sulphuric acid, for example the nitration reaction

The overall reaction is

$$HNO_3 + 2H_2SO_4 \iff NO_2^+ + H_3O^+ + 2HSO_4^-.$$

This reaction is similar to the reaction of acetate ions in sulphuric acid in that a weaker acid than the sulphuric acidonium ion is formed in each case

NaOOCCH₃ +
$$^{2}\text{H}_{2}\text{SO}_{4} \longleftrightarrow \text{Na}^{+} + \text{CH}_{3}\text{C(OH)}_{2}^{+} + ^{2}\text{HSO}_{4}^{-}$$
.

In contrast to the solvents treated so far, liquid ammonia makes available stronger bases than exist in aqueous solution but only relatively weak acids are available in ammonia. Liquid ammonia has a low self-ionisation constant available in ammonia. Liquid ammonia to a low self-ionisation constant (1 x 10^{-33} at -50° C) and an intermediate value of 22 at -33° C for the dielectric constant. Its self-ionisation reaction is represented by the equation:

$$2NH_3 \longleftrightarrow NH_4^+ + NH_2^-$$
.

The strongest base is the amide ion. Strong acids are levelled to the acid strength of the ammonium ion, the solvated proton in liquid ammonia. Acetic acid which is a weak acid in water exhibits the same acid strength

as hydrochloric acid and nitric acid in liquid ammonia:

$$CH_3COOH + NH_3 \longrightarrow NH_4^+ + CH_3COO^-$$

 $HCl + NH_3 \longrightarrow NH_4^+ + Cl.$

The reaction between ammonium chloride and sodium amide in liquid ammonia is equivalent to the neutralisation reaction of a strong acid with a strong base:

$$\mathrm{NH_4^{Cl}}$$
 + $\mathrm{NaNH_2}$ \longrightarrow 2 $\mathrm{NH_3}$ + NaCl .

Because of the strong basic property of ammonia, substances which do not act as an acid in aqueous solution can have acidic properties in ammonia. For example, acetamide is an acid in ammonia:

$$CH_3CONH_2 \iff NH_4^+ + CH_3CONH^+$$
.

Up to the present we have been dealing with solvents that are selfionised and the extent of their acid-base properties are determined by the respective acid and base properties of the solvent ions. But there is a large number of useful solvents which exhibit basic properties but no acid Such solvents include pyridine, acetone and other ketones and There is another group of important solvents, such as benzene, chloroform, pentane, whose acid-base properties are so weak that these properties cannot be detected by ordinary means. In discussions of acid-base phenomena these solvents are usually referred to as "inert", however acid-base reactions between solutes in these solvents can be demonstrated. The two beakers on the overhead projector contain colourless liquids, methanol and benzene. When we place a small quantity of picric acid, C₆H₂(NO₂)₃OH, into each of these solvents the solution of picric acid in benzene is colourless, the solution in methanol is yellow. The non-ionised molecule of picric acid is colourless and this is its state in benzene solution. In methanol the acid is ionised and the yellow colour is due to the picrate ion. When we add a small volume of methanol to the colourless benzene solution we see that a yellow solution is produced indicating that the methanol reacts directly with the picric acid in benzene solvent. This acid-base reaction may be represented by the following equation:

$$C_6H_2(NO_2)_3OH + CH_3OH \longrightarrow C_6H_2(NO_2)_3O^- + CH_3OH_2^+$$

When we add trichloroacetic acid to this yellow solution it becomes colourless again. Trichloroacetic acid is a stronger acid than picric acid and it reacts directly with the yellow picrate ion to reform picric acid:

$$\operatorname{CCl}_3^{}\operatorname{COOH} + \operatorname{C}_6^{}\operatorname{H}_2^{}(\operatorname{NO}_2^{})_3^{}\operatorname{O}^- \longrightarrow \operatorname{C}_6^{}\operatorname{H}_2^{}(\operatorname{NO}_2^{})_3^{}\operatorname{OH} + \operatorname{CCl}_3^{}\operatorname{COO}^-.$$

This demonstration shows that acid-base reactions can occur in benzene where there is no evidence to suggest that the solvent participates in the acid-base reaction.

We extended the acid-base theory of Arrhenius to media other than water by recognising that in acetic acid the base is the acetate ion, in sulphuric acid it is the hydrogen sulphate ion, and in ammonia it is the amide ion. We also added a solvent molecule to the bare proton to represent the hydrogen ion and to emphasise the difference in its acid strength from one medium to another. However, we cannot apply our modified Arrhenius theory to define acids and bases in inert solvents in which ionisation of acids by interaction with the solvent does not take place and where such ionisation is not a necessary pre-requisite to acid-base interaction in the solvent. In 1923, Brønsted in Denmark and Lowry in England proposed almost identical acid-base theories which classify as acid-base reactions all reactions involving the transfer of protons. This is a broader theory than our modified Arrhenius theory for it allows the classification of reactions between gases, solids, or solutes in inert solvents as acid-base reactions.

The Bronsted-Lowry Theory

Acid-base interaction in this theory is characterised by the transfer of a proton from combination with one reactant to combination with the other reactant. Acid-base interaction can be represented simply as:

$$Acid$$
, + $base_2$ conjugate conjugate $acid_2$ $base_1$

The substance from which the proton is transferred is the acid, the substance that takes up the proton is the pase. Let us summarise some of the important aspects of the Brønsted-Lowry theory:

- I. This theory emphasises the importance of the acid-base pair. The acid HA has a partner base A which it forms when it donates its proton to a stronger base. This partner base is called the conjugate base of the acid HA.
- 2. The theory relates the characteristics of acids and bases to the reacting molecules or ions in a way that is independent of the solvent. This theory can be applied to gaseous reactions where no solvents are involved; for example the reaction between hydrogen chloride gas and ammonia is a

Brønsted acid-base reaction.

$$HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4^+Cl_{(s)}$$

It applies to reactions in non-ionising solvents; for example, the picrate-trichloroacetic acid neutralisation in benzene solvent:

$$CCl_3COOH + C_6H_2(NO_2)_3O^- \longrightarrow C_6H_2(NO_2)_3OH + CCl_3COO^-$$

3. The part played by the solvent in determining acidity is clarified by the theory. Solvents can themselves act as acids or bases. Many solvents can act as an acid and as a base, others are virtually aprotic. In the dissociation of perchloric acid in anhydrous acetic acid, the solvent acts as a base:

$$\text{HClO}_4$$
 + $\text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{C(OH)}_2^+$ + ClO_4^- acid solvent (base)

In liquid ammonia, the solvent acts as an acid in the following reaction:

NaH + NH₃
$$\longrightarrow$$
 NH₂ + Na⁺ + H₂
base solvent (acid)

In water, as in the other self-ionising solvents, the solvent can act as an acid or a base. In the hydrolysis of the ammonium ion water acts as a base, but in the hydrolysis of ammonia water acts as an acid:

$$NH_4^+$$
 + H_2O \longleftrightarrow H_3O^+ + NH_3 acid solvent (base)

 NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^- base solvent (acid)

▶. The quantitative treatment applied to the Arrhenius acid-base equilibria can be applied with equal success to Brønsted acid-base reactions. The treatment can be used to express the relative strengths of an acid and its conjugate base. For example, the relationship of the acid strength of the ammonium ion to the base-strength of the ammonia molecule in aqueous solution is developed as follows:

$$K_a \text{ for } NH_4^+ = \frac{[H_3O^+] [NH_3]}{[NH_4^+]}$$
 $K_b \text{ for } NH_3 = \frac{[NH_4^+] [OH^-]}{[NH_3]}$

By combining these two expressions it is seen that the product of the dissociation constant of the acid and its conjugate base equals the ionic product of the solvent:

$$K_a \text{ for } NH_4^+ \times K_b \text{ for } NH_3 = [H_3O^+][OH^-]$$

= $K_w \text{ for } H_2O$

5. For reactions in a self-ionising solvent between an acid that is almost completely dissociated to give solvated protons (that is, a strong acid) and a base that does not react to any significant extent with the solvent (i.e. a weak base), the reaction may be represented as a direct interaction between the solvated protons and the molecules of the weak base; for between the solvated protons and the molecules as strong acid and ammonia example, the reaction in aqueous solution between a strong acid and ammonia may be represented by the following equation:

$$_{\mathrm{H_3O}^+}$$
 + $_{\mathrm{NH_3}}$ \longrightarrow $_{\mathrm{NH_4}^+}$ + $_{\mathrm{H_2O}}$

Compare this equation with the equation for the reaction of a strong acid with a strong base in aqueous solution:

$$_{\mathrm{H_3O}^+}$$
 + $_{\mathrm{OH}^-}$ \longrightarrow $_{^{2\mathrm{H_2O}}}$

It is evident that in the latter but not the former reaction water is the product of the reaction. In the workshop on stoichiometry you will compare these two reactions along with other acid-base reactions to find the volume changes in neutralisation reactions can be related to the quantity of water produced in the reaction.

6. Finally, a parallel can be drawn between proton-transfer and the electron-transfer half-reactions used to explain oxidation-reduction reactions. These half reactions take the following form:

In the equation for the neutralisation of ammonia the water shown on the right hand side of the equation may be considered to be present also as a reactant associated with the hydration of the proton.

For electron transfer

For proton transfer

Lewis Theory of Acids and Bases

Seven years before the Brønsted-Lowry theory appeared G.N. Lewis had published his theories of chemical bonding in which he introduced the idea of the covalent bond to explain the structures of non-ionic molecules. The formation of a molecule of hydrogen from two separate atoms is symbolised as follows:

In this representation the electrons are denoted by dots. The bond between the two atoms in the molecule is pictured as a pair of electrons shared between the atoms. This type of bond involving a shared pair of electrons Lewis called the covalent bond. Chlorine gas also exists as diatomic molecules. Each chlorine atom has seven electrons in its outermost electron shell and we think of a covalent bond being formed between two atoms by one of these electrons from each atom contributing to a pair to be shared by the two atoms. Representing only the electrons in the outermost shell we represent the electron-dot formula for a molecule of chlorine as follows:

The bonding between hydrogen and chlorine in hydrogen chloride can also be accounted for by a shared pair of electrons:

Molecular ammonia is represented by three hydrogen atoms covalently bonded to one nitrogen atom:

Lewis represented the reaction between hydrogen chloride and ammonia as follows:

He explained the proton transfer in terms of the competition for the proton between the pairs of unshared electrons on the nitrogen atom and the pair of electrons originally shared between the hydrogen and the chlorine. ammonia in this reaction is the base, a Lewis base is defined as an electron-pair donor. The proton is the Lewis acid, the electron pair acceptor. In Lewis's terms an acid accepts a share in a pair of electrons with the formation of a coordinate bond. This definition greatly extends the classification of acids, far beyond the hydrogen acids of the Arrhenius and Brønsted-Lowry theories. This extension was prompted by the fact that many substances that do not contain hydrogen undergo reactions similar to acids with indicators. Many of these substances are neutralised by compounds such as alcohols, esters and acid anhydrides; e.g. the two beakers standing on the overhead projector each contain a very small quantity of the indicator crystal violet. To the first we add a small volume of water and to the second a small volume of anhydrous chlorobenzene. We see that both solutions of the indicator are purple in colour. To the first beaker we add concentrated hydrochloric acid, to the second, anhydrous aluminium chloride. In each case the indicator is changed to a yellow colour. We represent the indicator colour change in aqueous solution as an acid-base reaction:

$$\begin{array}{ccc}
\text{H}^{+} & + & \text{In} & \longrightarrow & \text{H} : \text{In}^{+} \\
\text{acid} & \text{purple} & & \text{yellow}
\end{array}$$

The Lewis theory represents the colour change produced by the anhydrous aluminium chloride by a similar reaction:

Cl: Al + :In
$$\longrightarrow$$
 Cl: Al: In Cl yellow acid purple

When both the electrons in the pair which is shared between the two When both the electrons, the covalent bond formed is often atoms come from one of the atoms, the covalent bond or simply as a co-ordinate bond. referred to as a co-ordinate covalent bond or simply as a co-ordinate bond.

Now on adding aqueous sodium hydroxide solution to the hydrochloric acid solution the purple colour of the indicator is restored when sufficient alkali has been added to neutralise the acid. To the aluminium chloride solution we add a dilute solution of pyridine in chlorobenzene and we effect the same type of change. The purple colour of the indicator is restored. The Lewis theory explains this reaction also as a neutralisation reaction of the acid, aluminium chloride with the base pyridine:

This acid-base reaction is carried out in an aprotic non-ionising solvent and it does not involve the transfer of protons. Lewis writing on acid-base theories soon after the publication of the Brønsted & Lowry papers justly points out that "to restrict the group of acids to those substances which contain hydrogen, interferes as seriously with the systematic understanding of chemistry as would the restriction of the term oxidising agent to substances containing oxygen." *

The Lewis theory makes a substantial contribution to the systematic generalisation of chemical theory. However the Bronsted-Lowry theory also has made a worthwhile contribution to our understanding of quantitative aspects of acid-base theory particularly applied to non-aqueous media. Although in this article we extend the Arrhenius theory to explain the role of the solvent in determining the acid strength of a solute, historically the part played by the solvent was clarified as a result of the application of the Bronsted-Lowry theory to non-aqueous media.

Any atom, molecule, or ion that accepts a share in a pair of electrons to form a new covalent or co-ordinate bond acts as Lewis acid. Some examples of Lewis acid-base reactions follow:

Boron trifluoride reacting with ammonia:

$$BF_3 + NH_3 \longrightarrow F_3BNH_3$$
acid base

Mercury (II) iodide dissolved in excess iodide ions:

$$_{\mathrm{HgI}_{2}} + 2\mathrm{I}^{-} \longrightarrow \mathrm{HgI}_{4}^{2-}$$

Gaseous sulphur trioxide reacting with solid calcium oxide:

$$SO_3$$
 + CaO \longrightarrow CaSO₄ acid base

Self-ionisation of liquid sulphur dioxide:

dioxide:

$$2SO_2 \longrightarrow SO^{2+} + SO_3^{2-}$$

acid base

Self-ionisation of liquid dinitrogen tetroxide: $N_2O_4 \longrightarrow NO^+ + NO_3^-$

$$N_2O_4 \rightarrow NO^+ + NO_3^-$$
 acid base

Liquid sulphur dioxide and dinitrogen tetroxide are good non-aqueous, aprotic solvents with small but finite conductances resulting from the self. self-ionisation reactions represented above. These reactions are not unlike the self-ionisation reactions of sulphuric acid excepting in this case there there are no protons present. These liquids dissolve metals, form solvates, and no and react generally in a manner similar to the protonated self-ionising solvent solvents; for example, pyridine has been titrated conductometrically in liquid liquid sulphur dioxide with thionyl chloride (SOCl₂) which appears to act as a new control of the solvent. The Lewis interpretation of as a reasonably strong acid in this solvent. The Lewis interpretation of acids and because of the same category as water, liquid and bases includes these solvents in the same category as water, liquid ammonia, sulphuric acid and acetic acid.

In the stoichiometry workshop you will use the method of In the stoichiometry workshop of the the reaction in which ammonia displaces the water warration to examine the reaction. The nickel ion is the water molecules coordinated to the nickel ion. acting as a Lewis acid and the two bases, water and ammonia, are in competitions. the two sammonia molecules are added stepwise at competition for the acid.

the expense of water molecules. The overall reaction for the addition of six ammonia molecules is represented as follows:

$$\begin{bmatrix} H \\ \text{Ni}(:\text{O:H})_6 \end{bmatrix}^{2+} + 6:\text{N:H} \longrightarrow \begin{bmatrix} H \\ \text{Ni}(:\text{N:H})_6 \end{bmatrix}^{2+} + 6H_2\text{O}$$

The Lewis theory embraces a great number of substances. We have seen that Lewis acids include the molecules - AlCl3, BF₃, HgI_2 , SO_3 and the ions H^+ , NH_4^+ , SO^{2+} , NO^+ , Ni^{2+} and other metal ions. They also include the atoms N, O, S, C. Lewis bases include NH $_3$, CH $_3$ COCH $_3$, C $_6$ H $_5$ N, OH $^-$, Cl $^-$, SO_3^{2-} , NO_3^{-} . A Brønsted-Lowry acid is the neutralisation product of a Lewis acid-base reaction, the reaction between a proton and an anion; hydrochloric acid is not an acid in the strict sense of the Lewis theory. It is rather difficult to express the relative strength of Lewis acids and bases for there is no common criterion for all substances defined according to the Lewis theory. An attempt to arrange Lewis acids in order of increasing strengths meets with unexpected problems. For example, the silver ion is a Lewis acid, it combines with ammonia to form complexes which are much stronger than the hydroxyl complexes of silver. On this basis we would say that ammonia is a stronger base than the hydroxyl ion toward the silver ion. However when we compare the reactions of the proton with these two bases, again in aqueous solution, the order is reversed, the hydroxyl ion is much the stronger base.

Earlier we referred to the similarity in the representation of an electron transfer reaction and a proton transfer reaction but there is a much closer relationship between a Lewis acid-base reaction and an oxidation-reduction reaction. The difference between the sharing of a pair of electrons and the complete transfer of electrons, one by one, in oxidation reduction reactions is a difference of degree only. However if this next step in the generalisation of the classifications of chemical reactions of grouping Lewis acids with oxidising agents and Lewis bases with reducing agents is to be successful it should await a broader quantitative interpretation of the strengths of the species in the two classes. At present we measure the strength of acids relative to the basic strength measured relative to that of hydrogen.

The Lewis theory is based on experiment al facts and it provides the most universal application of the ideas of acids and bases; it embraces the whole of co-ordination chemistry and it furnishes a useful description of many organic reactions. It takes the correlation of reactions in non-aqueous media a step further than is achieved by the Bronsted-Lowry theory and it reveals a link between oxidation-reduction reactions and acid-base reactions that is worthy of further development.



WHAT WE CAN

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Freezing point measurements are particularly useful in studying chemical systems involving solvents other than water. This article describes the application of such measurements to solutions in sulfuric acid.

Much elementary inorganic chemistry is carried out in aqueous solution, and we first learn about acids and bases in relation to water as the solvent. In aqueous solution, an acid ionizes to form the hydronium ion H₃O+

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

and a base ionizes to give the hydroxide ion OH-

$$B + H_2O \rightarrow BH^+ + OH^-$$

Water is an amphoteric substance in that it can act as a base in accepting a proton from an acid HA, and it can also act as an acid by donating a proton to a base B. However, there

is a vast amount of fascinating chemistry associated with other solvents involving molecules and ions that in many cases do not exist in water. Many of these nonaqueous solvents resemble water in the sense that they also have both acid and base properties. Thus, in liquid ammonia, acids ionize according to the equation

$$HA + NH_3 \rightarrow NH_4 + A^-$$

and bases according to the equation

$$B + NH_3 \rightarrow BH^+ + NH_2^-$$

Although the idea that sulfuric acid can act as a base is somewhat surprising when we first meet it, sulfuric acid is an amphoteric solvent the same as water and liquid ammonia. Sufficiently strong acids can ionize in sulfuric acid by donating a proton to give H₃SO₄+

$$HA + H_2SO_4 \rightarrow H_3SO_4 + A$$

and many substances act as bases:

$$B + H_2SO_4 \rightarrow BH^+ + HSO_4^-$$

Acids and bases of the water and sulfuric acid systems are compared in Table I. Much of the

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FROM FREEZING POINTS

information on the behavior of solutes in sulfuric acid has been obtained from cryoscopic measurements.

The freezing point of a solvent is depressed

Table I. Comparison of Acids and Bases of the Water and Sulfuric Acid Systems

	Solvent	
Acids	H_2O	H ₂ SO ₄
Strong	H ₂ SO ₄ HCl HNO ₃	HB(HSO4)4
Weak	CF ₃ CO ₂ H (CO ₂ H) ₂ CH ₃ CO ₂ H	H₂S₂O₁ HSO₃F
Bases		70 H
Weak	NH3	CF ₃ CO ₂ H C ₆ H ₆ NO ₂ HNO ₃ CH ₃ CO ₂ H H ₂ O
	CH ₃ CO ₂	NH3 HSO4
Strong	OH-	. H504

by the addition of a solute by an amount proportional to the total number of solute particles (molecules or ions) that are formed in the solution. Strictly speaking, this is true only if the solution is ideal, which means that intermolecular and interionic forces between the solute species and between the solute and the solvent can be ignored. In solvents with relatively high dielectric constants—for example, water and sulfuric acid—interionic forces are small and useful information can be obtained from the freezing-point depression concerning ν, the number of particles (molecules or ions) formed when one molecule of solute is dissolved in a solvent. If T_0 is the freezing point of the solvent, and T, the freezing point of a solution containing m moles of solute per kilogram of solvent, then the freezing point depression, $\theta = T_0 - T$, is related to the molality of the solute m by the expression

 $\theta = \nu k_f m$

The cryoscopic constant, k_h , is a characteristic quantity for each solvent and is sometimes called the molal freezing-point depression con-

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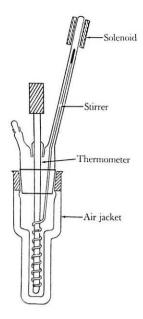


Figure 1. Cryoscope used for freezing-point determinations in $\mathrm{H}_2\mathrm{SO}_4$

stant because it is equal to the freezing-point depression of a 1-molal solution of a non-electrolyte. Thus, by measuring the freezing-point depression θ produced by a solute at a known concentration (molality), a value for ν may be obtained. For example, in aqueous solution the nonelectrolyte, sucrose, gives $\nu=1$; the binary electrolyte, NaCl, gives $\nu=2$; and the ternary electrolyte, Na₂SO₄, gives $\nu=3$ (see also Glossary, page 18).

Anhydrous (100%) sulfuric acid is a useful solvent for cryoscopic measurements because it has a convenient freezing point of 10.37° C. and a relatively high cryoscopic constant of 6.12. For comparison we may note that the cryoscopic constant of water is only 1.86. Thus a 1-molal solution of a nonelectrolyte depresses the freezing point of sulfuric acid by 6.12° or from 10.37° to 4.25° C. Generally it is convenient to measure a total freezing point depression of 1° to 3° C., and deviations from ideal behavior are smaller in more dilute solution. When a suitable mercury thermometer with a small range, or a platinum resistance thermometer is used, temperature measurements can be made to an accuracy of a few thousandths of a degree relatively easily. A suitable apparatus for freezing-point measurements in sulfuric acid is shown in Figure 1.

To measure the freezing point of a solution, the cryoscope is first cooled by immersing it in an ice bath until the solution has supercooled to about 2° C. below the expected freezing point. It is then placed in the air jacket and the temperature of the bath is adjusted to approximately 2° below the expected freezing point. It is then necessary to seed the sulfuric acid to induce crystallization: This can be done conveniently by dropping into the sulfuric acid a small piece of platinum wire that has been cooled in liquid air (Figure 2). Crystallization begins immediately and the temperature rises to the freezing point in two to three minutes and then remains almost constant. Because a certain amount of solid solvent crystallizes out on freezing, the concentration of the solution in equilibrium with the solid is slightly greater than the original solution that was made up. When necessary for accurate work, a correction for this can be applied.

Experimental results for a number of different solutes are given in Figure 3. Metal hydrogen sulfates give $\nu = 2$ because they are fully ionized binary electrolytes:

$$KHSO_4 \rightarrow K^+ + HSO_4^-$$

Many organic compounds also give very similar freezing-point depressions corresponding to $\nu=2$. This is because they behave as strong bases in this highly acidic medium and are fully protonated:

$$RNH_2 + H_2SO_4 \rightarrow RNH_3^+ + HSO_4^-$$

Amine

$$(CH_3)_2CO + H_2SO_4 \rightarrow$$

Ketone $(CH_3)_2COH^+ + HSO_4^-$

$$\begin{array}{c} CH_3CO_2H \,+\, H_2SO_4 \rightarrow \\ Carboxylic & CH_3CO_2H_2{}^+ \,+\, HSO_4{}^- \\ acid & \end{array}$$

$$CH_3CONH_2 + H_2SO_4 \rightarrow$$
Amide
$$CH_3C(OH)NH_2 + HSO_4 -$$

$$C_6H_5CO_2CH_3 + H_2SO_4 \rightarrow$$
Ester
 $C_6H_5C(OH)OCH_3 + HSO_4^-$

Water and phosphoric acid provide examples of inorganic compounds that ionize as simple bases giving $\nu = 2$:

$$H_2O + H_2SO_4 \rightarrow H_3O^+ + HSO_4^-$$

 $H_3PO_4 + H_2SO_4 \rightarrow H_4PO_4^+ + HSO_4^-$

Compounds that contain two basic groups may protonate on both groups: thus, o-phenyl-

 $C_{12}H_{22}O_{11}$ V=1 NaCl $H_{2}O$ $Na^{+}+Cl^{-}$ V=2 $Na_{1}SO_{4}$ $H_{2}O$ $2N_{1}+SO_{4}$ 3 particle V=3

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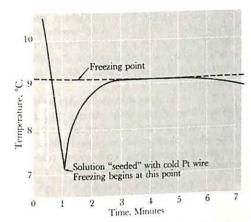


Figure 2. Typical temperature-time plot when the freezing point of a sulfuric acid solution is determined

enediamine gives $\nu = 3$, corresponding to the reaction

$$C_6H_4(NH_2)_2 + 2H_2SO_4 \rightarrow C_6H_4(NH_3)_2^{+2} + 2HSO_4^{-1}$$

Cryoscopic measurements have often enabled more complex types of ionization to be elucidated. A classic example is provided by nitric acid which was found to give $\nu = 4$. Clearly, this is not consistent with simple protonation

$$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$$

which gives $\nu = 2$; nor can it be explained by the much less likely acidic ionization of nitric acid

$$HNO_3 + H_2SO_4 \rightarrow H_3SO_4^+ + NO_3^-$$

or the very improbable diprotonation which would give v = 3:

ould give
$$\nu = 5$$
:
 $HNO_3 + 2H_2SO_4 \rightarrow H_3NO_3^{+2} + 2HSO_4^{-1}$

The only reasonable explanation of the observed ν value of 4 is the formation of the nitronium ion according to the equation

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

This reaction may be visualized as occurring in the following stages:

e following stages:

$$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$$

 $H_2NO_3^+ \rightarrow H_2O + NO_2^+$
 $H_2NO_3^+ \rightarrow H_2O_3^+ + HSO_4^-$

$$H_2NO_3^+ \rightarrow H_2O^+ + HSO_4^-$$

 $H_2O + H_2SO_4 \rightarrow H_3O^+ + HSO_4^-$

These cryoscopic measurements provided some of the first evidence for the existence of the nitronium ion as a stable species and thus gave an explanation for the efficiency of nitricsulfuric acid mixtures for aromatic nitration. In such a mixture the nitric acid is extensively

converted to the nitronium ion which is the strongest possible nitrating agent:

$$RH + NO_2^+ = RNO_2 + H^+$$

has same

election

patternas

.O.: C.: O.

 $C_6H_6+NO_2^+ \rightarrow bengene$

C₆ H₅ NO₂ + H⁺ netrobenzene

A large amount of additional supporting evidence for the nitronium ion has been obtained from spectroscopic and conductometric measurements and by the isolation of stable nitronium salts such as NO2+ClO4-.

Triphenylcarbinol also gives a v value of four and this can be explained only by an ionization exactly analogous to that of nitric acid:

$$(C_6H_6)_3COH + 2H_2SO_4 \rightarrow (C_6H_6)_3C^+ + H_3O^+ + 2HSO_4^-$$

Although many carboxylic acids give a v value of 2 as a result of simple protonation, mesitoic acid gives $\nu = 4$. This is again the result of a quite similar ionization giving a stable positive

$$CH_{3} \longrightarrow C$$

$$CH_{4} \longrightarrow C$$

$$CH_{5} \longrightarrow C$$

$$CH_{5} \longrightarrow C$$

$$CH_{5} \longrightarrow C$$

$$CH_{5} \longrightarrow C$$

$$CH_{6} \longrightarrow C$$

$$CH_{7} \longrightarrow C$$

$$CH_{7} \longrightarrow C$$

$$CH_{7} \longrightarrow C$$

$$CH_{7} \longrightarrow C$$

$$CH_{8} \longrightarrow C$$

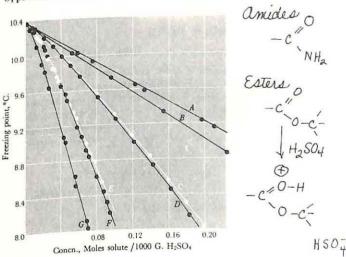
$$CH_{8} \longrightarrow C$$

$$CH_{8} \longrightarrow C$$

$$CH_{9} \longrightarrow C$$

$$CH_$$

Figure 3. Freezing points of some solutions in sulfuric acid. A, sulfuryl chloride (SO₂Cl₂); B, nitrobenzene (C₆H₆NO₂); C, sodium hydrogen sulfate (NaHSO₄); D, benzophenone [(C₆H₆)₂CO]; E, nitric acid (HNO₃); F, triphenyl carbinol [(C₆H₅)₃COH]; and G, potassium nitrate (KNO3)



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All the above ionizations are in fact special cases of a more general reaction of XOH compounds which can be written

$$XOH + 2H_2SO_4 \rightarrow$$

$$XHSO_4 + H_3O^+ + HSO_4^-$$

if the hydrogen sulfate formed is a nonelectrolyte and as

$$XOH + 2H_2SO_4 \rightarrow X^+ + H_3O^+ + 2HSO_4^-$$

if the hydrogen sulfate is ionized as in the above examples. Ethyl alcohol, which gives a ν value of three, ionizes according to the equation $C_2H_5OH + 2H_2SO_4 \rightarrow$

$$C_2H_5HSO_4 + H_3O^+ + HSO_4^-$$

Iodic acid behaves in a quite similar manner giving the nonelectrolyte iodyl hydrogen sulfate

$$HIO_3 + 2H_2SO_4 \rightarrow$$

$$IO_2HSO_4 + H_3O^+ + HSO_4^-$$

These reactions result from the fact that sulfuric acid has a very great affinity for water, converting it almost quantitatively to the H₃O+ ion. Even some anhydrides are further dehydrated by sulfuric acid according to the equation

$$X_2O + 3H_2SO_4 \rightarrow$$

XHSO4

formula of a hydrogen sulfate

$$2XHSO_4 + H_3O^+ + HSO_4^-$$

Thus, hexamethyldisiloxane gives $\nu=4$ which may be explained in terms of the ionization

$$[(CH_3)_3Si]_2O + 3H_2SO_4 \rightarrow$$

$$2(CH_3)_3SiOSO_3H + H_3O^+ + HSO_4^-$$

Dinitrogen pentoxide gives $\nu = 6$ and, bearing in mind the formation of the nitronium ion from nitric acid, this experimental result can be explained in terms of the ionization

$$N_2O_5 + 3H_2SO_4 \rightarrow$$

$$2NO_2^+ + H_3O^+ + 3HSO_4^-$$

which is quite analogous to the ionization of hexamethyl disiloxane except that the hydrogen sulfate formed—namely, nitronium hydrogen sulfate—is fully ionized. Dinitrogen tetroxide also gives $\nu=6$ as a consequence of the formation of both the nitronium and nitrosonium ions:

$$N_2O_4 + 3H_2SO_4 \rightarrow$$

$$NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$$

and KNO₃ gives $\nu = 6$:

$$KNO_3 + 3H_2SO_4 \rightarrow$$

$$NO_2^+ + K^+ + H_3O^+ + 3HSO_4^-$$

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Some very weakly basic substances such as nitrobenzene behave as weak electrolytes in sulfuric acid ($\nu=1.2$ to 1.3) while a few substances such as trinitrobenzene, $C_6H_3(NO_2)_3$, and sulfuryl chloride, SO_2Cl_2 , behave as non-electrolytes ($\nu=1$).

All the electrolytes discussed above behave as bases of the sulfuric acid system—they accept one or more protons and give rise to the corresponding number of hydrogen sulfate ions. An acid of the sulfuric acid system ionizes to give the characteristic cation H₃SO₄+

$$HA + H_2SO_4 \rightarrow H_3SO_4 + A^-$$

Cryoscopic measurements have shown that there are rather few acids of the sulfuric acid solvent system which, in view of the very weak basicity of sulfuric acid, is not particularly surprising. Thus, several substances which are strong acids in water, such as trifluoracetic acid, CF3CO2H, behave as nonelectrolytes in sulfuric acid giving $\nu = 1$. Chlorosulfuric acid, HSO₈Cl, similarly gives $\nu=1$. Perchloric acid is often regarded as the strongest inorganic acid; its solutions have not been studied directly, but the freezing-point depressions produced by salts such as NH4ClO4 and NaClO4 have been measured. In each case $\nu = 3$. If these perchlorates ionized as simple binary electrolytes as they do in water

$$NH_4ClO_4 \rightarrow NH_4 + ClO_4$$

then, of course, a ν value of 2 would be obtained. The only possible interpretation of the experimental observation that $\nu=3$ is that the perchlorate ion is protonated to give unionized perchloric acid:

$$NH_4ClO_4 + H_2SO_4 \rightarrow$$

$$NH_4^+ + HSO_4^- + HClO_4$$

This implies that perchloric acid is a very weak acid of the sulfuric acid solvent system and is ionized very little, if at all. Alkali metal chlorides are interesting because they give $\nu=5$. Here again protonation occurs, but in addition there is a further reaction to give chlorosulfuric acid:

$$NaCl + 3H2SO4 \rightarrow$$

$$Na^+ + H_3O^+ + HSO_3Cl + 2HSO_4^-$$

Chlorosulfuric

acid

This is confirmed by experiments on HCl which give $\nu = 3$

$$HCl + 2H2SO4 \rightarrow$$

$$HSO_3Cl + H_3O^+ + HSO_4^-$$

and on chlorosulfuric acid which is a non-electrolyte with $\nu = 1$.

Disulfuric acid gives a freezing-point de-

pression that is greater than that produced by a nonelectrolyte; for example, in a 0.1-molal solution $\nu = 1.3$. This indicates that disulfuric acid is partially ionized according to the equation

$$H_2S_2O_7 + H_2SO_4 = H_3SO_4 + HS_2O_7$$

A new and interesting acid of the sulfuric acid solvent system was discovered as the result of cryoscopic measurements on solutions of boric acid and boric oxide which were both found to give $\nu=6$. It was suspected from earlier work that boron trihydrogensulfate, $B(HSO_4)_3$, might be the product of the reaction between boric acid and sulfuric acid. The equations for the formation of $B(HSO_4)_3$ from boric acid and boric oxide, respectively, would be

$$B(OH)_3 + 6H_2SO_4 \rightarrow B(HSO_4)_3 +$$

 $3H_3O + 3HSO_4^- (\nu = 7)$
 $B_2O_3 + 9H_2SO_4 \rightarrow 2B(HSO_4)_3 +$
 $3H_3O^+ + 3HSO_4^- (\nu = 8)$

which are not in agreement with experiment. However, if we remember that $B(HSO_4)_3$ is likely to be a very good acceptor molecule as is BF_3 , and that, therefore, by analogy with the known reaction $BF_3 + F^- \to BF_4^-$ we might write $B(HSO_4)_3 + HSO_4^- \to B(HSO_4)_4^-$, then the above equations can be rewritten in the form

$$B(OH)_3 + 6H_2SO_4 \rightarrow$$
 $B(HSO_4)_4^- + 3H_3O^+ + 2HSO_4^ B_2O_3 + 9H_2SO_4 \rightarrow 2B(HSO_4)_4^- +$
 $3H_3O^+ + HSO_4^-$

In both cases $\nu=6$ in agreement with experiment. Perhaps the most interesting aspect of these results is that they prove the existence of a stable anion that is not solvolyzed by the sulfuric acid solvent. Hence, the acid corresponding to this anion, HB(HSO₄)₄, must be a strong acid of the sulfuric acid solvent system. Solutions of the free acid can be prepared by adding boric acid to oleum (H₂S₂O₇ in H₂SO₄), in which case the freezing point at first rises and the freezing-point composition curve has a slope that corresponds to the net loss of two particles: $\Delta \nu = -2$ in accordance with the equation

$$H_3BO_3 + 3H_2S_2O_7 \rightarrow$$
 $\nu = 3 \times 1.3 = 3.9$
 $H_3SO_4 + B(HSO_4)_4 - H_2SO_4 \text{ (solvent)}$
 $\nu = 2$
 $\Delta \nu \sim -2$

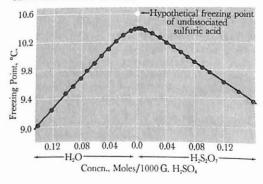
Although cryoscopy is a powerful tool for the investigation of solutions in ionizing solvents, it is not always possible to deduce the mode of ionization of a solute unambiguously just from the cryoscopic determination of the value of v. In such cases, other experimental techniques such as conductometry and spectroscopy must be used to provide supplementary data. However, even the cryoscopic method itself can be extended to provide, in addition to the number of particles formed, some information concerning their nature by using as a solvent not 100% H-SO4 but sulfuric acid containing a small amount of water or disulfuric acid. It will have been noted above that one of the products in many of the ionizations is water in the form H₃O+. HSO₄-. In such cases confirmatory evidence that water is indeed one of the products can be obtained by carrying out cryoscopic measurements in dilute oleum, when the initial freezing-point depression produced by the solute will be smaller than the depression produced by the same solute in 100% H2SO4. For example, when nitric acid is added to oleum, the freezing point actually rises initially, which means the depression is negative. This is in accordance with the fact that the water produced removes H2S2O7 to form sulfuric acid and the overall reaction may be represented as follows:

HNO₃ + 2H₂S₂O₇
$$\rightarrow$$

 $\nu = 2 \times 1.3 = 2.6$
NO₂⁺ + HS₂O₇⁻ + 2H₂SO₄
 $\nu = 2$ $\Delta \nu = -0.6$

The freezing-point curve of the water-sulfur trioxide system in the region of the composition H_2SO_4 is shown in Figure 4. That portion of the curve at the left shows the freezing-point de-

Figure 4. Freezing points of solutions of water and sulfur trioxide in sulfuric acid



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pression produced by a solution of water in sulfuric acid and the portion at the right shows the freezing-point depression produced by sulfur trioxide. When water is added to 100% H₂SO₄ the first additions produce a negligible depression of the freezing point which means that the freezing-point composition curve is flat at the maximum and has zero slope. As the concentration of water is increased, the slope of the freezing-point curve gradually increases until it reaches its final constant value.

This initial curvature is due to the selfionization of the solvent. It is well known that pure water is slightly ionized in the following manner:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

and at 25° C., $[H_3O^+] = [OH^-] = 10^{-7}$ m. This self-ionization results because water possesses both acid and base properties. Because of its amphoteric nature, sulfuric acid undergoes a similar but much more extensive self-ionization according to the equation

$$2H_2SO_4 \leftrightharpoons H_3SO_4^+ + HSO_4^-$$

and at 25° C., $[H_3SO_4^+] = [HSO_4^-] \sim 1.5 \times 10^{-2}$ m. In addition, sulfuric acid undergoes another type of self-dissociation reaction according to the equation

$$2H_2SO_4 \leftrightharpoons H_3O^+ + HS_2O_7^-$$

and at 25° C., $[H_3O^+]=[HS_2O_7^-]\sim 7~\times 10^{-3} \mathrm{m}.$

When a solute is added to sulfuric acid which gives rise to one or more of these self-dissociation ions, one or both of the above equilibria are shifted to the left; that is, the self-ionization is repressed, so that the net increase in the number of particles in solution is less than the number added. Water which ionizes to give ${\rm H_3O^+}$ and ${\rm HSO_4^-}$ shifts both of the above equilibria to the left and thus initially the loss of particles by the repression of the self-dissociation equilibria almost compensates for the additional



RONALD J. GILLESPIE, chairman of the chemistry department at McMaster University, Ontario, Canada, received his Ph.D. degree in 1949 from University College, London. He was a Commonwealth Fund Fellow at Brown University, Providence, R. I., from 1953 to 1954 and was awarded the Harrison Memorial Medal of the Chemical Society in 1954.

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GLOSSARY

Cryoscopy: The determination of freezing points produced in liquids by dissolved substances in order to determine molecular weights of solutes and certain properties of solutions

Cryoscopic Constant: Molal freezing-point depression constant. Depression of freezing point produced by 1 mole of solute in 1 kilogram of solvent. It may be shown by means of thermodynamics that the cryoscopic constant is related to the heat of fusion of the solvent, ΔH_f , by the expression

$$k_f = \frac{R \ T_1^2 \ M}{10^8 \ \Delta H_f}$$

where M is the molecular mass of the solvent

Cryoscope: Instrument for measuring freezing points

Binary: Involving two entities

Ternary: Involving three entities

Oleum: H2S2O7 in H2SO4

particles added, and the freezing point curve starts with a very small slope. When sufficient water has been added, the self-dissociation equilibria are almost completely repressed and the freezing-point curve then becomes almost linear with a slope corresponding to the formation of two particles, H_3O^+ and HSO_4^- . The initial curvature of the freezing-point curve is also evident for all the electrolytes in Figure 3.

Similar remarks apply to the repression of the self-dissociation equilibria by disulfuric acid. From the shapes of the freezing-point curves given by H₂O and H₂S₂O₇ and by other solutes that repress the self-dissociation, quantitative information on the self-dissociation equilibria can be obtained. From the total concentrations of the self-dissociation products the freezing point of a hypothetical undissociated sulfuric acid may be calculated to be 10.625° C. This illustrates another use of cryoscopic measurements in sulfuric acid

In interpreting freezing-point measurements in 100% H₂SO₄, repression of the self-ionization must be allowed for or, alternatively, if results of the highest accuracy are not required, it is adequate to repress initially the self-ionization equilibria by the addition of a small quantity of a suitable solute such as water, providing that the solute under investigation does not react with the added water.

Suggested Reading

- (1) Gillespie, R. J., Robinson, E. A., "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, p. 386, Academic Press, 1959.
- (2) Sisler, H. H., "Chemistry in Nonaqueous Solvents," Reinhold, New York, 1961.

4. Organic chemistry and biochemistry

4. Chimie organique et biochimie

Many schools now teach organic chemistry although the time devoted to this branch of the subject may vary greatly in different schools. All too often, however, it is presented as a collection of a great deal of factual information about the preparation, properties and reactions of a large number of compounds. The initial enthusiasm which students display when they hear about organic substances familiar in everyday life unfortunately evaporates as they become overwhelmed by the volume of information. A modern course in organic chemistry demands a clear rethinking of the traditional approach and an attempt to provide a correlating theme for the discussion of a limited range of compounds. Many courses still 1 still begin by discussing methane and its preparation by the dry distillation of sodium acetate—a specialized reaction with a complicated mechanism. Textbooks still contain examples of react reactions which are either wrong or which only work with reasonable yields for particular members of a homologous series.

REACTION MECHANISMS

The article by H. R. Christen describes the way in which the teaching of organic chemistry has been modernized in a Swiss Oberrealschule. The extended time devoted to organic chemistry has been obtained by a drastic reduction in the time spent on descriptive inorganic chemistry. Dr. Christen's course includes a detailed discussion of reaction mechanisms in organic chemistry, but he points out the danger of discussing theoretical topics when the pupils do not know very much about the properties of the reacting substances. Most teachers have experience of pupils who can discuss sophisticated theories in detail but who do not know whether a quite common chemical is a solid, liquid or gas at room temperature. Dr. Christen's course on mechanisms is therefore preceded by an alweek course in which he presents a condensed review of the more important types of compound, illustrated by as many

La chimie organique est maintenant enseignée dans de nombreuses écoles, bien que le temps consacré à cette branche de la chimie varie considérablement selon les établissements. Trop souvent, toutefois, cette matière se présente sous forme d'une longue énumération d'informations concrètes concernant la préparation, les propriétés et les réactions d'un grand nombre de composés. L'enthousiasme que les élèves commencent par montrer, lorsqu'ils entendent parler de substances organiques qui leur sont familières parce qu'ils les rencontrent couramment dans la vie quotidienne, se dissipe malheureusement à mesure qu'ils sont submergés par la masse des informations. Un cours de chimie organique moderne exige une révision fondamentale, selon des lignes de pensée claire, de la conception traditionnelle de cette discipline et un effort en vue de trouver un thème commun pour l'étude d'un nombre limité de composés. De nombreux cours débutent encore par l'étude du méthane et de sa préparation par distillation à sec de l'acétate de sodium, réaction très particulière dont le mécanisme est complexe. On continue à trouver dans les manuels des exemples de réactions qui ou bien sont fausses ou bien ne donnent des rendements appréciables que pour certains composants particuliers d'une série homologue.

MÉCANISMES DE RÉACTION

Dans son article, H. R. Christen décrit la façon dont l'enseignement de la chimie organique a été modernisé dans une « Oberrealschule » suisse. Afin de pouvoir consacrer plus de temps à la chimie organique, le temps affecté à la chimie minérale descriptive a été très fortement réduit. Le cours du Dr Christen comprend l'examen détaillé des mécanismes de réaction en chimie organique, mais l'auteur souligne le danger qu'il y a à étudier des questions théoriques alors que les élèves n'ont que des notions très vagues sur les propriétés de substances en réaction. La plupart des enseignants pourraient citer le cas d'élèves capables d'exposer en détail des théories très complexes mais qui ne savent pas si, à la température ambiante, un corps chimique des plus communs se présente sous forme solide, liquide ou gazeuse. C'est pourquoi le cours du Dr Christen sur les mécanismes est précédé d'un

experiments and samples as possible. The Oberrealschule curriculum has a strong scientific content, and the depth of this particular course may be greater than some teachers would wish at school level. Few teachers, however, would disagree with Dr. Christen's view that it is necessary to devote much more time to organic chemistry than is customary nowadays.

ORGANIC EXPERIMENTS

The article by C. Heyer and W. Rannow emphasizes the value of quantitative experiments in organic chemistry at the school level. They describe simple, inexpensive apparatus which can be used for a wide variety of experiments. The experiments on the temperature coefficient of viscosity of an oil and the distillation of fuel oil have an obvious and valuable link with industry. The piston syringe for measuring gas volumes is a feature of many modern school courses in practical chemistry, and the article shows how useful this piece of apparatus can be in a variety of organic experiments.

The properties of unsaturated hydrocarbons are usually illustrated by a demonstration preparation of ethylene and its reaction with bromine water and alkaline permanganate solution. H.-J. Jakowatz points out that the normal preparation must be carried out by the teacher because of frothing problems and the dangers of hot, concentrated sulphuric acid, and that a poor yield of very impure product is obtained. The preparation of propylene, however, is safe, rapid and produces gas of very high purity. It can easily be made by the pupils themselves. The method described for the determination of the composition of propylene by quantitative combustion on copper oxide provides another example of the value of the gas syringe in quantitative experiments.

BIOCHEMISTRY IN SCHOOL COURSES

Some of the most spectacular advances in natural science in the last fifty years have been in the field of biochemistry, yet this subject rarely finds a place in the school curriculum. K. Müntz in the article reproduced here points out that nature is the biggest chemical factory on earth, providing most of the substances needed for human nourishment and many raw materials for industry. The chemistry of living organisms should therefore be included in the school curriculum. The article suggests that the principles of biochemistry can be introduced, without great changes in the syllabus, if biochemical examples are used in chemistry and biology courses wherever they are appropriate. Dr. Muntz discusses the mechanisms of biological oxidation and reduction. The article is particularly valuable in that it first discusses the topic in detail for the benefit of the teacher, and then gives a simplified. shorter account for presentation in class. In this way students

cours de huit ou neuf semaines dans lequel il passe brièvement en revue les types de composés les plus importants en illustrant ce cours par le plus grand nombre possible d'expériences et d'échantillons. Le programme d'études de $\Gamma\alpha$ Oberrealschule » fait une place importante aux sciences et ce cours, en particulier, est sans doute plus approfondi que certains enseignants ne le jugeraient utile au niveau scolaire. Mais rares sont ceux qui ne seront pas d'accord avec le D^r Christen pour penser qu'il faudrait consacrer à la chimie organique beaucoup plus de temps qu'il n'est d'usage de le faire actuellement.

EXPÉRIENCES DE CHIMIE ORGANIQUE

Dans leur article, Ch. Heyer et W. Rannow soulignent la valeur des expériences quantitatives de chimie organique à l'école. Ils décrivent des appareils simples et peu coûteux qui peuvent servir à des expériences extrêmement variées. Les expériences sur le coefficient de viscosité d'une huile en fonction de la température et sur la distillation de fuel-oil présentent des liens évidents et utiles avec l'industrie. La seringue à piston destinée à mesurer le volume des gaz figure dans de nombreuses écoles modernes parmi les appareils utilisés pour les travaux pratiques de chimie et l'article montre combien cet appareil peut être utile pour diverses expériences de chimie organique.

Les propriétés des hydrocarbures non saturés sont généralement illustrées par la démonstration de la préparation de l'éthylène et de sa réaction avec de l'eau de brome et une solution alcaline de permanganate. H.-J. Jakowatz souligne que la préparation usuelle doit être effectuée par le maître, en raison des problèmes que pose la formation d'écume et des dangers que présente l'emploi d'acide sulfurique concentré à chaud; en outre, on n'obtient qu'une très faible quantité d'un produit très impur. Au contraire, la préparation du propylène ne comporte pas de danger, elle est rapide et donne un gaz d'une très grande pureté. Elle peut être facilement réalisée par les élèves eux-mêmes. La méthode indiquée pour la détermination de la composition du propylène par combustion quantitative sur oxyde de cuivre fournit un autre exemple de l'utilité de la seringue à gaz dans les expériences quantitatives.

COURS DE BIOCHIMIE A L'ÉCOLE

Au cours des cinquante dernières années, c'est dans le domaine de la biochimie que quelques-uns des progrès les plus spectaculaires des sciences physiques et naturelles ont été réalisés; néanmoins, cette matière trouve rarement une place dans les programmes scolaires. Dans l'article reproduit ici, K. Müntz fait remarquer que la nature est la plus grande usine chimique du monde et fournit la plupart des substances nécessaires à l'alimentation humaine ainsi que de nombreuses matières premières pour l'industrie. C'est pourquoi la chimie des organismes vivants devrait être inscrite aux programmes. L'article montre qu'on pourrait présenter les principes de la biochimie, sans bouleverser les programmes, en faisant appel à des exemples biochimiques toutes les fois que cela convient dans les cours de chimie et de biologie. Le Dr Müntz examine les mécanismes de l'oxydation et de la réduction biologiques. L'article est particulièrement précieux du fait qu'il expose

can relate what they know about oxidation and reduction, fatty acids and carbohydrates, catalysis etc., to the importance of these reactions and substances in living systems.

LARGE MOLECULES

One of the editor's objectives in this volume has been to include a few "definitive" articles for use as reference material by teachers so that they can extend and bring up to date their knowledge of various topics. The article by F. Danusso on "Building Macromolecules" presents a contemporary account of the elements of polymer science by a member of the distinguished school of Italian polymer chemists.

Attention might also be drawn here to some useful experiments on the subject of large molecules which are described in Nuffield Chemistry: The Basic Course, 1966, London, Longmans, p. 370. Details are given for simple class experiments under the headings: The breakdown of starch; Can glucose be broken down further?; Can ethanol also be broken down further?; Cracking petroleum; Preparing soaps and detergents from castor oil; Breaking down and building up Perspex; Making nylon.

d'abord la question en détail, à l'intention du maître, et donne ensuite un compte rendu simplifié et plus court qui peut être présenté en classe. De cette façon, les élèves peuvent établir un lien entre ce qu'ils savent de l'oxydation et de la réduction, des acides gras et des glucides, de la catalyse, etc., et l'importance de ces réactions et de ces substances dans les organismes vivants.

GROSSES MOLÉCULES

L'un des objectifs du directeur de la publication en ce qui concerne le présent volume a été d'y faire figurer quelques articles « définitifs » auxquels les enseignants puissent se référer pour augmenter et mettre à jour leurs connaissances sur diverses questions. L'article de F. Danusso sur la construction des macromolécules (« Building macromolecules ») présente un compte rendu de l'état actuel de la science des polymères, rédigé par un membre de l'éminente école italienne des chimistes des polymères.

Il convient aussi d'appeler l'attention du lecteur sur quelques expériences utiles concernant la question des grosses molécules, qui ont été décrites dans Nuffield chemistry. The basic course, p. 370, Londres, Longmans, 1966. On y trouvera des explications sur la façon de réaliser en classe des expériences simples, sous les titres suivants: « la décomposition de l'amidon; peut-on pousser plus loin la décomposition du glucose?; peut-on pousser plus loin la décomposition de l'éthanol?; le cracking du pétrole; la préparation de savons et de détergents à partir de l'huile de ricin; la décomposition et la construction de perspex; la fabrication du nylon ».

EXPERIENCES IN TEACHING ORGANIC CHEMISTRY

by H.R. Christen

I have tried to develop and modernise the teaching of organic chemistry at our Oberrealschule (scientific gymnasium) in a way based on the experience of other teachers and especially on discussions with my colleagues in Zurich. Although this paper applies only to teaching at the Oberrealschule (scientific background) I also hope that colleagues who teach in a classical gymnasium may be stimulated by my proposals.

First - the time available. At the Oberrealschule in Winterthur we have altogether six year-lessons reserved for chemistry; i.e. 3 lessons per week in the 3rd Class (11th school year), 2 lessons per week in the 4th Class and finally 2 lessons per week in the 5th Class (which takes only half a year). Formerly I was not able to devote more than 5 - 6 months for the teaching of organic chemistry. However, by rigorously shortening the descriptive inorganic chemistry - i.e. by restricting it to general chemistry - I am now able to spend a year or more on organic chemistry alone. This abundant time tempts one to a discursive treatment of the subject or to the enumeration and description of a vast amount of material in detail - a mistake which I committed some years ago. Student reaction to such teaching was mostly the same: firstly, great interest because they hear about many substances and chemical reactions already known from their everyday life, but the initial pleasure soon disappears because there was no real 'thread', no real synopsis of a huge mass of facts. It therefore seems very important to me that - even when there is plenty of time available - one should not lose oneself in the thicket of over a million organic substances, but should rather teach some selected groups of compounds correlated into a uniform picture by reference to reaction mechanisms, physical properties and so on. It was rather hard for

me to find the right proportions and a reasonable approach, and I also feel that not all the problems of teaching organic chemistry have been solved. The experiences of the last few years show, however, that a certain restriction in descriptive chemistry coupled with a simple but logical theoretical background stimulates the interest of most students.

Some years ago my syllabus followed a traditional path: the single types of compounds and their characteristic properties and reactions were treated in turn. In starting organic chemistry it is possible to take ethanol as an example and discuss it in detail (elementary analysis, determination of molecular mass and structure) or - more theoretically - to clarify of molecular mass and structure) or - more theoretically - to clarify the concept of functional groups (with appropriate experiments). If there is only a minimum amount of time available for organic chemistry this discussion of the functional groups may give a good survey of the different types of organic compounds.

But it seems self-evident to me that we cannot be limited to descriptive Organic chemistry. In my opinion it is clear that the results of modern theoretical organic chemistry really must be incorporated into the syllabus. The way in which this is done depends very much on the teacher, of course, and on the status and interests of the classes as well. carefully thought out, however, in order not to practice a sort of 'blackboard chemistry'. How, for example, can reaction mechanisms be taught if the students have no knowledge of the reacting substances? some time, therefore, I have followed up the introductory lessons with a condensed review of the more important classes of substances: hydrocarbons, alcohols, ethers, aldehydes, ketones, carboxylic acids, amines. review takes 8-9 weeks; since it is the foundation for later instruction it is essential to show as many experiments and substances as possible. Various reactions will then be only demonstrated but not explained; interest in least in learning more about reaction mechanisms will be stimulated by giving references to the very different conditions for apparently similar reactions (e.g. This 'synopsis' of substances will also give the students some links with materials already known in everyday life, and makes makes possible some valuable applications of general chemical principles (inter-(intermolecular forces, hydrogen bonds, strengths of acids and bond changes) character) formerly illustrated by inorganic examples.

This fundamental descriptive chemistry gives the foundation for further selected chapters. I therefore give next a rather detailed course (5-7 weeks)

on the general types of reaction mechanisms. In my experience insight into mechanisms, into interrelations between bond character and structure and reaction type, also the discussion of different factors influencing organic reactions are of great interest to students. Of course one can branch out into different topics depending on the time available or on the interests of the students; topics such as aromatic substitution (explanation of the rules of orientation), distinction between $\rm S_{N}^{1-}$ and $\rm S_{N}^{2-}$ mechanisms and between the factors which favour the first or second type, concepts such as cryptoions, transition state, kinetic or thermodynamic control and so on can be treated in secondary school classes without difficulty. Fortunately some excellent laboratory experiments are available (c.f. Selected Experiments in Organic Chemistry, Helkamp-Johnson, Freeman, San Francisco, 1964).

Sections which now may be attacked deal with high polymers, detergents and their structure and function, dyestuffs, biochemistry and so on. By means of these topics it is possible to appeal especially to the type of student who has technological or biological interests. My last class was particularly interested in stereochemistry (this surprised me) and in future years I will try to extend the treatment of this topic (discussion of the steric course of reactions, steric hindrance, asymmetric synthesis).

I fully realise that the customary scope of secondary school chemistry will be transgressed if organic chemistry is taught in the way I have described above, But is it not of much more interest to a schoolboy to hear something about properties and reactions of substances already known to him (e.g. gasoline, alcohol, benzene, acetone, vinegar, synthetic resins, polyethylene) than to learn the preparation and properties of sulphuric or nitric acid? And is it not much easier to exemplify the principles of general chemistry by using organic examples? How little is yet known, for example, about mechanisms of inorganic reactions and how difficult it is to explain the methods of investigating these mechanisms! just at this point where organic chemistry offers not only a more simple It is certainly but also a more lucid and clearer picture. I think it is much more useful to discuss some important types of reactions such as the S_N^{1-} or S_N^{2-} mechanisms rather thoroughly, to work out the mechanism, the influence of catalysts, the steric course, than to teach descriptive chemistry as an end in itself. It is my strong conviction that it is necessary to devote much more time to organic chemistry than is nowadays customary; an expenditure of a third of the total teaching time seems to me to be a

It is clear that the problems of teaching organic chemistry will not be solved for a long time yet, and I am sure that the construction of my own syllabus will change frequently in the future. Some questions with which I am constantly preoccupied are, for example, the use of the orbital model as well as the Kimball model, the use of the very practical concept of the formal charge. The orbital model is indispensible if one wants to But is it necessary to do give a pictorial representation of mesomerism. this in secondary school teaching? Is it not enough to clarify the concept of mesomerism (resonance) without giving a picture of electron distribution? Is it not difficult for the student to handle two models? How and when should the orbital model be introduced? Will not the student find it difficult to appreciate the concept of the formal charge - used so frequently in the literature? How can the student be taught to understand that, e.g., in the H₃O⁺ ion it is the oxygen atom (which is the most electronegative one) Which carries the formal charge of +1? Does a student grasp the meaning of the word "formal"? These are some questions to which I do not today know I think that these and other problems will only be solved after a period of experimenting with different ways of presenting organic chemistry in schools.

The penetration of teaching with rather extensive theoretical ideas demands a corresponding laboratory course. In my own case only about 14 of the total of 38 laboratory periods (2 lessons a week) are devoted to general and inorganic chemistry. Recently I have even omitted qualitative analysis (cation separation); instead we carry out simple experiments in organic analysis (identification of functional groups, identification of suitable substances by means of derivatives, separations of simple mixtures). I have received much valuable stimulus from the book by Helkamp and Johnson already cited; examples are the investigation of the kinetics of a S. 1. $^{\rm S}$ N¹- reaction (hydrolysis of methyl iodide) or the identification of the products in a substitution of an - OH group by a HCl/HBr mixture in a prime Preparations such as a Grignard reaction (preparation of triphenylcarbinol) or the aldol addition are also very suitable as start primary and a tertiary alcohol. as student laboratory exercises. If qualitative reactions and, especially, prepared to the prepared to the student laboratory exercises. preparations are done on the small scale (Grignard reaction in a 100 ml two-restance). two-necked flask) one will save so much time that preparation and purif: purification of a single substance can be completed in four lessons, even when the When the preparations are a bit more ambitious as in Friedel-Craft and Grime s are a pit more can be seen that the preparation of a substance starting from relatively simple materials is an exciting

experience for the student (the experience of 'creative' work). At a later date I hope to introduce modern methods of separation and identification (gas chromatography, spectroscopy) which I have postponed because I am not yet skilled in these techniques or because we do not have the necessary apparatus.

In this paper I have tried to show the possibilities and the problems of teaching modern organic chemistry. If the paper stimulates some colleagues to think about organic chemistry and its aims and its place in teaching its object will have been fulfilled.

SIMPLE QUANTITATIVE SCHOOL EXPERIMENTS IN ORGANIC CHEMISTRY

by Charlotte Heyer and W. Rannow

Quantitative experiments have a high educative value. For various reasons they are not used extensively in chemistry. The authors report the carrying out of quantitative experiments in schools which have resulted in more effective teaching. Simple experiments are described involving alkanes, alkynes, alcohols, fatty acids and esters. The possibilities of doing quantitative work in organic chemistry are demonstrated.

Introduction The high educational value of quantitative experiments has been referred to in several recent publications. It is well known (Klein, ref. 1) that quantitative experiments are rarely used as demonstrations in school experimental work. We hope to stimulate the introduction of simple, quantitative school experiments in organic the introduction of simple, quantitative school experiments in organic chemistry. Most of these are also suitable for demonstration purposes. In this case it is desirable to use the apparatus suggested by Klein.

Experimental and technical requirements The apparatus and the chemicals for the experiments described here can be made from readily available components or can be bought cheaply.

Gas measuring instruments: Carbon dioxide is frequently evolved in organic reactions and its volume can conveniently be measured with a gas syringe. This is readily available and needs no sealing with a gas syringe. This is readily available and needs no sealing with a gas syringe. This is readily available and needs no sealing with a gas syringe. These syringes are available liquid. In our experience, however, these syringes are available liquid. In our experience, however, these syringes are available in sufficient quantity at only a few schools. A burette can be made in sufficient quantity at only a few schools. A burette can be accurated as shown in Figure 1 and this has the advantage of into a gas burette as shown in Figure 1 and this has the advantage of into a gas burette as shown in Figure 1 and this has the advantage of the burettes at their dispodal. low cost. Most schools have sufficient burettes at their dispodal. low cost. Most schools have sufficient burettes at their dispodal. The burette can that of the gas syringe. The burette can be measuring devices are needed. be combined with the gas syringe when two measuring devices are needed. be combined with the gas syringe when two measuring devices are needed. The disadvantages of the burette are its complicated method of operation, the necessity of a suitable confining liquid for water-soluble gases, the necessity of a suitable confining liquid for water-soluble gases, and the need to take account of the vapour pressure of water.

The arrangement described in (2) embodies the principles of the gas measuring device described by Arendt and Dormer (3). It is

robust and cheap, but rather less suitable for semi-micro techniques. Transfer of the collected gas into another reaction vessel is rather difficult.

Apparatus for measuring liquid volumes: Apart from the burette, measuring cylinder and graduated semi-micro test-tubes we also recommend the 1ml pipette with a suction attachment (4) which permits the measurement of small volumes with adequate accuracy.

Other apparatus: Apart from the usual semi-micro apparatus, heating blocks have also been found useful. The block described in (4) permits easy and accident-free operation. The use of such things as hot concentrated sulphuric acid in heating baths is thus avoided. Because of the small sample size, boiling points can be determined with practically no risk of fire, and inexperienced school children can rapidly obtain accurate data.

Clocks with a central seconds hand are adequate for time measurements.

Chemicals: The chemicals used should be AR grade if possible since impurities play a greater role on the semi-micro scale than they do on the macro scale. When possible, weighing is replaced by volume measurement. This usually gives more precise results in a shorter time. In addition, the teacher has less work because less preparation is involved. The preparation of standard solutions, requiring a precision balance, is only needed in a few cases.

QUANTITATIVE EXPERIMENTS ON ALKANES

The emphasis in the experiments in this section is on demonstrating regularities in the properties of homologous series. These are also valid for the substances studied in subsequent sections and facilitate the systemization of knowledge. They form a basis for the study of natural phenomena. It is true that these problems can also be approached by studying tables of data, or by a lecture from the teacher. However, our work has shown that the retention of knowledge, the level of attainment and the general educational effect in the usual sense are noticeably higher than by conventional methods. Using statistical methods of analysis (the t - test)we have shown that differences are significant in general at the 5% level and sometimes at the 1% level.

The determination of boiling points, melting points and viscosity

has already been described in (4). The data obtained can be evaluated in different ways. Sources of error can be discussed in an elementary way and the necessity for making a series of measurements can be mentioned. Lastly, a diagram can be drawn in which measured values are compared with theoretical ones. In our experience the students' data scatter about the theoretical value as mean, so no correction was necessary.

The temperature dependence of viscosity can be simply demonstrated using the universal heating block. Paraffin oil or lubricating oil is heated to different temperatures in a 25ml beaker on the water-bath. At the same time the block is brought to the same temperature. The hot oil is poured rapidly into the viscometer and the viscosity deduced from the flow time. The values obtained are plotted as a function of temperature.

At this point an important connection with technology can be established. The question can be asked: what is the technical importance of the temperature dependence of viscosity? Give examples in which temperature dependence of viscosity plays a role.

The apparatus developed by Klein (1) for density measurement has been further simplified by us for use in school experiments. It can be used to determine the density of alkanes.

Two 20 - 30cm glass tubes of internal diameter 5 - 7 mm are connected to a Y-piece by short lengths of rubber tubing, and a rubber suction bulb is attached to the third limb of the Y. Each tube dips into suction bulb is attached to the third limb of the Y. Each tube dips into suction bulb is attached to the third limb of the Y. Each tube dips into suction bulb is attached to the third limb of the Y. Each tube dips into suction bulb is attached to the third limb of the Y. Each tube dips into the liquid a 25ml beaker containing, respectively, distilled water and the liquid a 25ml beaker containing, respectively, distilled water and the liquid under investigation. The liquids are sucked up the tubes to a height under investigation. The required density is determined with the help of a set-square. The required density is determined by simple proportion (density of water = 1). It is necessary obtained by simple proportion (density of water = 1). It is necessary obtained by simple proportion (density of water = 1). It is necessary obtained to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupils into the habit of always putting the unknown liquid to get the pupil

Distillation of fuel oil (boiling curve): H. Herbig (5) has described the measurement of a boiling curve on the semi-micro scale. Our experience shows the following method to be suitable. A test-tube with a side arm is closed with a bung carrying a thermometer. The side arm

is connected by rubber tubing to a bent delivery tube as shown in Figure 2. (The two ends of the glass tubing must be in contact inside the rubber tubing). Boiling stones are necessary to prevent bumping. A graduated semi-micro test-tube, cooled in water, is used as a receiver. The condenser tube must be wrapped with moist filter paper to prevent the light fractions from escaping. The fuel oil is heated gently until boiling begins and then is slowly distilled. The thermometer is read for every 0.5ml of distillate. The results are displayed graphically and discussed with the pupils. The technical consequences are gone into, and the significance of changes in the slope of the curve is discussed (different proportions of high and low boiling components).

Preparation of methane from aluminium carbide: The well known method of preparing methane from aluminium carbide can be simply related to stoichiometric calculations. We recommend a ($16\,\mathrm{mm}$ x 160mm) test-tube with a side arm. We have abandoned the use of semi-micro test-tubes with side arms since they vary markedly in dimensions and are very sensitive to mechanical or thermal shock. The tube is closed with a stopper carrying a pipette controlled by a spring clip (see (4)). This pipette reaches down to within 2cm from the bottom of the tube. Connection to a gas syringe or other gas measuring device is made with rubber tubing. Enough ${\rm Al}_4{\rm C}_3$ to cover the tip of a spatula is placed in the tube and 0.1ml water added from the pipette. The mixture is carefully warmed. If the heating is too strong the water evaporates before the reaction is complete. The volume of methane generated is read off at the end of the reaction when the apparatus has cooled to room temperature. For conversion of this volume to NTP we refer to the tables contained in (6). Each pupil has a photocopy of these tables.

The volume of gas produced is then compared with the theoretical value and the yield is expressed as a percentage of the theoretical. In our experience the theoretical yield cannot be obtained.

If Al₄C₃ is not available commercially it can be made by a method suggested by Ehringhaus (7). Powdered charcoal and aluminium powder in the ratio 3:1 are mixed in a porcelain crucible and heated strongly until the mass is glowing. Stirring is to be avoided. We obtained a product which contained charcoal as an impurity but which was good enough for methane preparation.

Further experiments: The following experiments can also be performed: determination of flash points and measurements of the melting point of paraffin as described in (4). Molecular weights can also be determined and simple element (C, H) analysis carried out.

Quantitative preparation of acetylene: The familiar preparation of acetylene from calcium carbide, like the preparation of methane from aluminium carbide, can be carried out quantitatively in essentiallythe same apparatus. It seemed desirable to suspend the calcium carbide in a non-aqueous dispersing medium such as benzene or toluene. In this way water is dispersed into droplets before it reaches the carbide. The loss of water by evaporation as a result of the heat evolved in the reaction is also reduced. If the acetylene is collected in a gas burette its solubility must be taken into account. The amount of acetylene obtained depends on the care with which the experiment is done and the quality of the calcium carbide. Before the experiment we can crush the carbide in a vice to increase its surface area. In our experiments the amount of gas collected was always less than the theoretical.

This example shows how quantitative experiments can be related to (or combined with) the usual qualitative ones. The gas collected can be examined with respect to colour, smell, solubility in water and propanone, flammability and in its reactions with substances which reveal unsaturation. Using a spring clip, the gas measuring apparatus can be detached from the generator. It is then fitted with a bent delivery tube which dips into water, propanone or Baeyer's reagent. On opening the clip the acetylene reacts with these substances. The gas must be released into a test-tube and ignited to demonstrate flammability because the original container may not necessarily be free from air. The fact that the gas for these qualitative tests has already been prepared in the quantitative experiment means that practically no additional time is required. If enough balances are available one can work from a known weight of calcium carbide rather than from a measured volume of water. In this case the purity of the calcium carbide must be determined.

QUANTITATIVE EXPERIMENTS ON ALCOHOLS

By using alcohols as examples pupils can learn in an elementary way how the formula of an organic substance is determined. Whereas this has previously been done by demonstration experiments, we have replaced these with class experiments quite successfully. In this case also, statistical analysis showed a significant difference in performance between an experimental class and a control group.

ween an experimental class carbon and hydrogen is based on that
Our method for determining carbon as the experimental

of E. Rossa (8). We used methanol as the experimental substance. To save time (especially preparation time) we carried out the carbon to save time (especially properties and the hydrogen determination determination in a class experiment and the hydrogen determination as a demonstration.

Considerably simpler, and equally applicable, is the method of Meyer, which can be used with volatile liquids (e.g. methanol) without needing the heating required by the Rossa method. The experimental arrangement is described in the older textbooks: a 500ml flask is connected to a gas measuring device. The size of the flask should not be much less than 500ml otherwise a saturated vapour is produced. We closed the flask with a two-hole stopper through which the previously mentioned pipette was inserted. (Figure 1).

0.05ml methanol are dropped into the flask and after a few minutes (if the gas measuring device shows that no further change can be detected) the quantity of vapour can be determined. The only difficulty encountered by our pupils was that of making the apparatus gas tight. We recommend the use of stopcock grease to give a good seal on the rubber tubes and taps. Soft red rubber stoppers should be used. We obtained results which agreed essentially with the theoretical values.

The results of molecular weight determinations on liquid alkanes were considerably less satisfactory. Further investigation (gasliquid chromatography) showed that commercial samples of alkanes (pentane, hexane, heptane, octane) are not sufficiently pure. In this case, the teacher should establish, by preliminary experiments, whether he available materials are good enough for use in these experiments.

The hydrogen atom of the OH group in alcohols can be replaced by alkali or alkaline earth metals. This enables conclusions to be drawn about the structure of alcohols. Text books describe a qualitative experiment on this. However, this does not show that only one hydrogen atom (for a monohydric alcohol) is replaceable by a metal. For this to be demonstrated the volume of hydrogen liberated must be measured. Thespecialist literature gives conflicting reports on this. W. Kintoff and R. Wagner (12) indicate that the reaction between alcohols and sodium does not occur quantitatively, but that adducts are formed which are not decomposed until heated to 900 °C. Th. Theimann (13), on the other hand, describes experiments which give quantitative results in a short time. We have checked this information and have used calcium and barium as well as sodium. We have also varied the experimental conditions to obtain optimum yield. This showed that the volume of gas evolved depended on the degree of subdivision of the metal. The most suitable procedure was arrived at by following the instructions given in 'Organikum' (14).

Preparation: Toluene is placed in a thick-walled flask containing a few shavings of sodium and is heated to boiling (110.6°C). The toluene must be dry, alternatively it must be dried over sodium. The molten sodium (mp 97.7°C) is then broken up by vigorous shaking into a grey-white suspension in the toluene. A coarse-grained

which is rapidly obtained is not sufficient! When the suspension is cooled it should not be stirred as this would cause the sodium particles to coalesce. The usual precautions for handling inflammable liquids and sodium mustbe observed. The suspension will keep for a long time provided that atmospheric moisture and oxygen are excluded.

Conduct of the experiment: 2ml of the suspension of sodium in toluene is placed in the apparatus after thorough shaling. 0.1ml alcohol is then added from the spring-clip pipette. There is a vigorous reaction at first which soon subsides. The lower part of the test-tube is then carefully warmed. The upper part should be kept cool to act as a reflux condenser. This causes the sodium to be well stirred by currents which mix it well with the other reagents. In this way the reaction is kept going. After 5 - 15 minutes (depending on the alcohol) the reaction is complete. After cooling the volume of hydrogen is measured and corrected to NTP.

The sodium suspension remaining can be used again with another alcohol, We obtained excellent results for all monohydric alcohols from methanol to pentanol.

One can calculate the mass of alcohol used knowing the density. Simple proportion then gives the molar ratio of hydrogen and alcohol. Simple proportion then gives the molar ratio of hydrogen and alcohol. It is then shown that 0.5 moles of hydrogen are evolved from 1 mole of alcohol, i.e. one hydrogen atom in the alcohol is replaced by sodium. Structural conclusions can be drawn from this. The experiment must Structural conclusions can be drawn from this. The experiment must be completed by identifying the hydrogen.

Since the quantities of sodium involved are very small, we have no Since the quantities of sodium involved are very small, we have no compunction about introducing this as a pupils experiment in well-disciplined classes. Residues are disposed of by pouring them into disciplined classes. Residues are disposed by the teacher, or, methylated spirit. This should be supervised by the teacher, or, methylated spirit. In no circumstances should residues be better, performed by him. In no circumstances should residues be better, performed by him. In no circumstances are explosion hazard.

As an additional experiment illustrating the gradual change of Properties in a homologous series, the miscibility of alcohols with Properties in a homologous series. The pupils then learn that the hydrophilic Water can be investigated. The pupils the molecular weight increases. Influence of the OH group is reduced as the molecular weight increases.

Conduct of the experiment: 1ml of water is placed in a graduated semi-micro test-tube. Alcohol is then added from the spring-clip semi-micro test-tube. For exact spipette until a cloudiness remains after shaking. The results can be pipette until a cloudiness remains indicated above. For exact tabulated and evaluated along the lines indicated above. Work the volume contraction must be taken into account.

QUANTITATIVE EXPERIMENTS ON FATTY ACIDS

In our treatment of the teaching of the fatty acids, as with the other groups referred to previously, we have emphasised the regularities to be observed as one ascends the homologous series. Here again it was shown that quantitative class experiments led to a noticeable increase in the pupils performance. In order to obtain comparable and sufficiently accurate results one must have acid solutions of equal concentration. We allow the pupils to use the spring-clip pipette to add 0.075ml of 55% formic acid, 0.12ml acetic acid, 0.15ml propionic acid and 0.18ml butyric acid in 1ml water to give approximately 2N solutions. pH values were determined using universal indicator paper. The results were presented graphically as a function of the number of carbon atoms. One sees that butyric acid is more strongly dissociated than propionic acid (c.f the pK values: propionic acid 4.87, butyric acid 4.82). The reason for this irregularity cannot be gone into in class. In order to clarify the concept 'acid strength' for the students and to illustrate the relation between acid strength and number of carbon atoms, we carried lut reactions of the acids with base metals. From the different rates at which the metals dissolve, i.e. the different rates of hydrogen evolution, the relative strengths of the acids can be determined. A suitable metal which gives good results in a reasonable time, turnedout to be magnesium.

In heterogeneous reactions the surface of the reagents plays an important role. Pieces of magnesium of similar shape are conveniently obtained frommagnesium ribbon. However, this has not been available commercially for a number of years. We got round the problem by using commercial magnesium turnings which we divided into pieces of equal size.

Use of indicators for determining end-points: A mixture of lml water and an organic acid (the quantity given above) was placed in a test-tube with a side-arm. This was suspended in a 100ml Erlenmeyer flask filled with water as a constant temperature bath. A drop of phenolphthalein solution was added to the acid.

The start of the reaction was taken as the time when the magnesium turnings were added to the solution. The end-point was given by the colour change. The magnesium is prevented from sticking to the wall of the tube by continuous shaking or stirring.

For butyric acid the time taken for the reaction exceeds that of the normal instruction period, and this is a problem. We should also say that the results have such a large scatter that we can only regard this as a semi-quantitative experiment. However, it has the advantage of clarity and simplicity.

The following variant is more difficult to perform, but more sensible in time requirements. In the apparatus shown in Figure 3, acid of the concentration given above is added to an excess of magnesium under 1ml water. An indicator is necessary only if it is desired to measure the total hydrogen evolved. If a burette is used as the gasmeasuring device the meniscus in the burette must be kept aligned with that in the levelling vessel. Temperature regulation can be controlled by a water bath. Volume readings are taken at fixed time intervals of one or two minutes. To obtain data on several acids we operate duplicate sets of the same apparatus simultaneously. All results are tabulated on the board and worked out by all the class. The results are represented graphically.

This type of experiment can also be used to measure the temperature dependence of reaction rate, by changing the temperature of the water bath. It can also be established by experiment, or the conclusion can be reached by reasoning, that the same volume of nydrogen is evolved in all cases when the acid is completely consumed. Finally, the hydrogen

We have carried out the quantitative neutralisation of fatty acids is identified. by carbonate in the following way. Using the apparatus of Figure 3, 0.075ml formic acid or 0.12ml acetic acid were dropped onto an excess of carbonate (Na₂CO₃ or K₂CO₃). We do not recommend the use of the higher acids low. On calculating the mean volume of carbon dioxide generated and converting this to NTP, practically theoretical values are obtained (the (theoretical 22.4ml, experimental 22.31ml). At the end of the experiment the gas is bubbled through calcium hydroxide solution and

The reducing properties of formic acid can be evaluated quantitatively so identified as carbon dioxide. by the permanganate method. However, the titrimetric method is complicated and scarcely allows the product to be identified as carbon dioxide by volume. In the dioxide. We therefore determine the carbon dioxide by volume. In the apparer apparatus of Figure 3, 1ml of 2N sulphuric acid (not concentrated) is dilar is diluted with 1ml water and a spatula-tip of potassium permanganate. is added. On gentle warming no gas should be evolved. The permanger manganate must be completely dissolved otherwise the result obtained is too! is too high. 0.075ml formic acid is added from the spring-clip pipette pipette and the mixture is then gently warmed. The carbon dioxide evolved in the mixture is then gently warmed with lime water. evolved is collected, measured and later identified with lime water.

Often 4 Often the reaction is stopped too soon, when low results are obtained.

Our results Our reults were only slightly below the theoretical value. The reducing property properties of formic acid are then related to its structure in the usual way. The reaction of conc. formic acid with conc. sulphuric acid can be carried out in the following simple, quantitative way very successfully. 1ml of conc. sulphuric acid is warmed gently in the apparatus shown in Figure 3, and 0.075ml 85% formic acid is then added. The liberated carbon dioxide is collected in the gas syringe. Only small volumes of gas are evolved and the apparatus must be completely gas tight. The experiment must be done either in a fume cupboard or with good ventilation. Students should only be allowed to do this experiment when they have acquired sufficient skill and when discipline is good enough. Otherwise we recommend this as a demonstration experiment. In class experiments we obtained an average volume of 43.8ml, the theoretical value being 44.8 ml. The carbon monoxide is identified by the blue fame it gives on burning, and it is simultaneously rendered harmless in this way.

In addition to the above experiments we have also measured and evaluated the boiling points, viscosoties, miscibilities with water and densities of the first four fatty acids.

QUANTITATIVE EXPERIMENTS ON ESTERS

One of the purposes of class experiments is to clarify the concept of 'reaction time' and to illustrate the laws of chemical equilibrium. We tried to find the optimum conditions for the formation of various esters. As a result of our literature study we chose ethyl acetate, pentyl acetate and ethyl butyrate as suitable preparations. We varied the temperature, concentration of reactants, catalysts (inorganic acids, ion exchange resins), methods of water removal, used heating baths, boiled under reflux and used various methods for working up the products.

We found the following to be the simplest and most rational procedure:-a mixture of 2ml ethanol and 0.5ml sulphuric acid was placed in a test-tube with side arm on a suitable heating bath (containing water or conc. calcium chloride solution). The mixture was heated to boiling and a mixture of 1ml ethanol and 1ml organic acid was slowly added dropwise. The condenser tube previously mentioned now acts as a reflux condenser (see(5)). After fifteen minutes the tube was rotated into a position suitable for the distillation of the mixture. The distillate was washed with sodium carbonate solution and then with water. It was separated from aqueous residues in a separating funnel and dried over calcium chloride for at least one day. The pupils stored their product in labelled, sealed-off test-tubes. In the next period the product was distilled (as in Figure 2) and the yield was calculated from the density and volume of the product. As an indication of purity, the boiling point was finally determined (see (4)).

We determined the temperature dependence of the esterification reaction in the following way:- in the course of esterification the amount of organic acid consumed is a measure of the extent of the reaction, and this can be determined by titration.

Conduct of the experiment: A mixture of 0.5ml sulphuric acid, (2N), 0.5ml organic acid and 0.5ml alcohol is diluted with 25ml water and titrated against 2 N caustic soda solution, using phenolphthalein as indicator. This gives the initial total acid concentration (time = 0. amount of ester = 0). At the same time a semi-micro water bath is brought to the desired temperature (e.g. 30°, 50°, 70°C.). Each group of pupils (or technicians) fill three semi-micro test-tubes with a mixture of 0.5ml organic acid and 0.5ml 2N sulphuric acid, and three further tubes with 0.5ml ethanol. The tubes are brought to the desired temperature in the water bath, the acid mixture is added to the alcohol and the time noted. It is important to prevent water from the water bath from getting in to the test-tubes. After 10, 20 and 30 minutes one reaction mixture is poured quickly into 25ml water in a 100ml Erlenmeyer flask. This effectively stops the esterification reaction. The residual acid concentration is then determined by titration against 2N caustic soda solution, using phenolphthalein as indicator. It is desirable to work in parallel groups using different esters at different temperatures. The results of all experiments are tabulated on the board and evaluated by all the pupils. In the simplest case one can simply plot the volume of 2N caustic

soda required against time, the temperature being noted. soda required agams. The graph must be plotted in such a of the curves differ markedly. The graph must be plotted in such a of the curves differ that the amount of ester is increasing with time.

Way that it is clear that the actor is possible / i way that it is clear that of the ester is possible (due account being A calculation of the yield of the ester is possible (due account being A calculation of the years acid catalyst) but it is not absolutely necessary. taken of the sulphuric acres to the curves should be discussed, and the The general trend shown by the curves should be discussed, and the The general trend shown by do we see from the results that question should also be asked: how do we see from the results that question should also be asked. The reached at a particular temperature? chemical equilibrijm has been reached in the titration. chemical equilibrium has been are needed in the titrations). One can (Equal amounts of caustic soda are needed in the titrations). One can (Equal amounts of causine by changing the initial conditions, e.g. by also modify the experiment by changing the influence of the catalyst also modify the experiment. The influence of the catalyst on reaction starting with excess alcohol. The influence of the catalyst on reaction valocity can also be demonstrated.

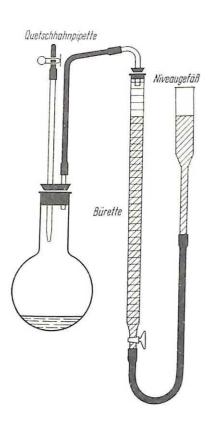
CONCLUDING REMARKS

We have tried, with some success, to give quantitative experiments We have tried, with some and have tried to get our pupils to make the character of problems, and practical experience and the character of problems. the character of propieties, and practical experience and to use of their previous knowledge and practical experience and to

participate actively in the theoretical and practical preparations for the experiments as well as in the calculations and writing up of the results. We asked additional questions on the results to encourage the pupils to think independently, as indicated above. We also asked: what errors could have affected the results? What further experiments are necessary to allow an unambiguous conclusion to be drawn? What general laws do the results establish? Without going further into detail we can summarise by saying that the introduction of these experiments into the course has justified itself. The expense in time and materials was not excessive. A class which performed these experiments achieved better results than a control class.

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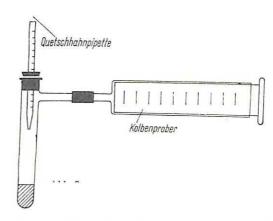


Fig. 3. Semi-micro gas generator with measuring syringe

Fig. 1. Determination of molecular weight of readily volatile substances using gas burette

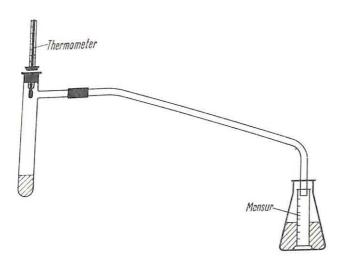


Fig. 2. Semi-micro distillation apparatus

PROPYLENE

AN EASILY PREPARED UNSATURATED HYDROCARBON

by H. - J. Jakowatz

Ethylene is generally used to demonstrate the properties of an unsaturated hydrocarbon. It is of course obvious that we should begin by looking at the first member of the homologous series. This can be done in schools without any difficulty because ethylene is easily prepared and it has a tendency to react immediately with many other substances. If one has the time to set up the apparatus, ethylene can be prepared and examined by the students themselves in practical classes.

Unfortunately, when we come actually to use ethylene there are considerable difficulties. Olefines are usually prepared from alcohols using concentrated sulphuric acid, and in the preparation of ethylene we must use ethanol. The ester which is formed during the reaction decomposes under the conditions of the experiment into ethylene and sulphuric acid. The final result is the separation of one mole of water from one mole of alcohol. The reaction goes most easily with tertiary alcohols(i.e. the 'branched' alcohols). It goes less readily with secondary alcohols and only with considerable difficulty with the primary alcohols, one of which is ethanol. The conditions and yields for these reactions with tertiary, secondary and primary alcohols are as follows:-

(a) Tertiary Alcohol

$$CH_3CH_2CCH_3$$
 $00 - 95^{\circ}C$ $CH_3CH = CCH_3$ 84% yield

2-Methylbutanol-2

2-Methylbuten-2

(b) Secondary Alcohol

(c) Primary Alcohol
$$CH_{3}CH_{2}OH \xrightarrow{160-170} CH_{2} = CH_{2} \qquad 21\% \text{ yield}$$
Ethanol
Ethylene

As can be seen quite clearly, ethanol as a primary alcohol needs by far the highest temperature and the greatest concentration of sulphuric acid to get a yield which at most is only 21% ethylene. Sulphuric acid to get a yield which at most is only 21% ethylene. Sulphuric acid to get a yield which at most is only 21% ethylene. Sulphuric acid one can overlook the small percentage yield of tendency to froth. One can overlook the small percentage yield of tendency to froth. One can overlook the small percentage yield of tendency to froth. One can overlook the small percentage yield of tendency to froth. One can overlook the small percentage yield of tendency to froth. One can overlook the small percentage yield of tendency to froth. One can overlook the small percentage yield of tendency to froth. One can overlook the small percentage yield of tendency to froth. One can overlook the small percentage yield of tendency to froth. One can overlook the small percentage yield of tendency to frother, and the gas evaluable. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available. Much more sulphuric acid - are cheap chemicals readily available.

temperature needed to bring about the reaction, 170°, causes the sulphuric acid to oxidise and carbonise considerable amounts of the organic material. Not only is it disadvantageous that the mixture turns a dark colour soon after the start of the reaction (towards the end the whole of the seething mixture is jet black!) but the ethylene also contains carbon monoxide and sulphur dioxide. The difficult dehydration of ethanol thus produces ethylene gas with a smell which is considerably affected by the presence of ether and sulphur dioxide, and which is poisonous because of the presence of carbon monoxide. Because of these impurities it cannot be used to determine the molecular weight of ethylene. Finally, there is a carbonised residue which forces the student to assume that there are certain undesirable side-reactions which cannot be followed up. It is true that wecan get rid of the sulphur dioxide by washing with a 4 N solution of sodium hydroxide, and we can absorb the ether in concentrated sulphuric acid. Kintoff (Ref. 3, II, 116 footnote 2)here recommends setting up two successive wash-bottles of concentrated sulphuric acid as a precaution. One cannot, however, get rid of the carbon monoxide at all. Quite apart from the fact that it is poisonous, the fact that its molecular weight is the same as that of ethylene means that we get correct but deceptive results when we determine the molecular weight of the gas. The teacher should avoid such conscious deceptions.

Recognising this awkward situation, Kintoff (3, 116) suggests that pure ethylene should be bought to use in the molecular weight experiment. R. Burger (ref. 4) has adopted Gattermann's idea and uses concentrated phosphoric acid rather than sulphuric acid for the dehydration. This latter method produces good yields without any noticeable by-products. However, the anhydrous phosphoric acid needed cannot be bought; it has to be nade by heating the 85-89% acid on a sand-bath to 210 - 220 °C. This means that the experiment takes longer to perform and this is not very desirable in the practical class situation.

It therefore seemed important to look for an olefine which could be used in schools and which could be prepared more easily. Propylene as the next member of the homologous series was the obvious choice. Since 2-propanol is a secondary alcohol it reacts more readily than 1-propanol and was therfore the preferred choice of the two alcohols. According to Fieser (ref. 1) a 75% solution of sulphuric acid was apparently sufficient to dehydrate 2-propanol. Powdered copper sulphate was used as a catalyst. The reaction should

take place as follows at a temperature of 100°C.:-

There was, at the first attempt, no appreciable frothing worth mentioning at 100 °C and a great quantity of a colourless sweet-smelling gas was liberated. Nor was there any darkening of the reaction mixture. Even after boiling for a considerable time the colour always remained a light green-blue. When the source of heat was removed gas evolution quickly ceased, but when reheated more gas was readily evolved. The propylene produced rapidly decolourised an aqueous solution of bromine and an alkaline solution of potassium permanganate.

Encouraged by this success, further, more thorough experiments were carried out with the results given below. In order to obtain greater quantities of the gas, direct heat (i.e. without the use of greater quantities of the gas, direct heat (i.e. without the use of wire gauze, asbestos mat or sand-bath) was applied to the vessel, wire gauze, asbestos mat or sand-bath) was applied to the vessel, wire gauze, asbestos mat or sand-bath) was applied to the vessel, wire gauze, asbestos mat or sand-bath) was reached. In and in a few minutes the necessary temperature was reached. In about 5 minutes some 5 litres of propylene passed into the gas-holder. Experiments, then, which require larger quantities of gas are Experiments, then, which require larger quantities of gas are easily and quickly carried out under these conditions. The molecular easily and quickly carried out under these conditions. The molecular weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was found to be 43 when a sample which had not been weight was

combustion period of only 7 - 8 minutes there is a threefold volume increase. It is known that the volume is unchanged on combustion of a gaseous hydrocarbon containing one carbon atom; there is a volume doubling when there are 2 carbon atoms, and a threefold increase when there are 3 carbon atoms since carbon dioxide takes the place of the hydrocarbon. This, of course, only obtains when a solid oxidising agent is used, and when there is complete condensation of the water formed:

$$C_3^{H_6}$$
(gaseous) + 9O (as CuO) \longrightarrow 3CO₂ (gaseous) + 3H₂O (1)
1 volume 3 volumes

From this experiment the fact that there is an exactly threefold volume increase can be clearly seen. This fact, and the value of the molecular weight obtained, prove how very pure the propylene is.

Since the ethylene molecule is completely symmetrical it must be polarised before addition reactions can occur. This is why an addition reaction with ethylene is more difficult than with propylene. Propylene possesses a natural polarity arising from the asymmetric nature of the molecule; the methyl group pushes a partial negative charge to the other end of the molecule (ref, 5, 21-22):

$$CH_3 - CH = CH_2$$
3 2 1

Thus C 1 is always negative and ready to combine with a positive ion (e.g. Br), and C 2 becomes a carbonium ion and then adds a negative ion (e.g. Br). This is why the double bond in propylene is more reactive than that in ethylene. This is seen in the more rapid decolourisation of bromine water and change of colour of alkaline permanganate solution. Both quantitative and preparative additions to the molecule are easily carried out. Thus in a few seconds 1 litre of propylene in a flask absobs an added, previously calculated, quantity of bromine to form colouless 1.2-dibromopropane. On the other hand, the corresponding preparation with ethylene takes thirty minutes. Furthermore the volume of ethylene cannot be accurately measured because of its gaseous impurities.

The reaction between chlorine and propylene requires compicated apparatus and it takes a considerably longer time without having any advantage over the use of bromine. The chlorine addition reaction should therefore only be carried out in small practical classes.

From what has been said above it is clear that propylene is much better than ethylene for demonstrating the chemical properties of an olefine. There is the following slight disadvantage, but it is only slight, namely the somewhat more complicated formula for propylene. However this is more than outweighed by the more rapid and cleaner preparation of this gas and the ease with which it reacts. On the other hand, should the teacher feel that he must use ethylene for demonstration purposes, this should not prevent the use of propylene in the students practical classes, even if only one hour is available for the lesson. Students who have only had little practice can propare propylene in a very short time with very simple apparatus, and can examine its properties as an unsaturated hydrocarbon (see below). Using only a 75% concentration of sulphuric acid avoids most dangers, and since there is very little frothing the experiment can be carried Out using a 100 ml Erlenmeyer flask. There is no danger from any highly poisonous carbon monoxide since the gas is so pure, and there is no need of even the most simple form of purifying apparatus. Since the gas can be obtained so quickly the student can fill four large testtubes (28 x 200) in less than two minutes and use them to perform any subsequent reactions. In addition to all this, the student who has already probably seen experiments demonstrated with ethylene and is now himself using propylene is encouraged to compare the two methods and to conduct his own research as to the cause of the various differences.

It should be a principle of our chemistry teaching that we should not disguise any possible difficulties which might occur in carrying not disguise any possible difficulties which might occur in carrying out experiments. However, the experience I have had in experiments out experiments. However, the experience I have had in experiments with propylene should be made full use of. Those experienced teachers with propylene should be made full use of. Those experienced teachers who, on the quiet, have been continually frustrated by the inadequacies who, on the quiet, have been continually frustrated by the inadequacies of our work on ethylene will, like the present author, not hesitate to make use of its sister compound propylene, which is easier to work with.

Experimental

1. Preparation of Propylene.

(a) In large quantities as a demonstration

of concentrated acid to one volume of water) together with a teaspoonfull of powdered copper sulphate or fine sea-sand are heated together in a 500 ml round-bottomed flask to 100 °C (thermometer!). While the gas is being formed large bubbles appear but the liquid never froths dangerously. If the heat is turned down slightly the temperature can be kept almost constant. Without a wash-bottle a 5 litre gas-holder can be filled in five minutes (it is possible to fill several smaller holders if necessary). The gas smells pleasantly sweet and is therefore completely free from sulphur dioxide and most probably free from carbon monoxide and other products (see experiment 3).

(b) In smaller quantities for students' practical work

A 100 ml Erlenmeyer flask is filled with 11 ml of a mixture consisting of 5 parts (by volume) of 2 - propanol and 6 parts of 75% concentration sulphuric acid and a pinch of copper sulphate or sea-sand. The flask is clamped to a stand (no thermometer). After heating the flask over an open spirit flame (!) the gas is lead off through a delivery tube into a pneumatic trough. Four to five test-tubes, acting as reaction vessels, are filled. The gas is then tested for smell, combustibility, (also when mixed with air), its reaction with bromine water and with alkaline permanganate solution. Total time for the experiments is 20 minutes. If there are not enough test-tubes available the students can, of course, remove the burners and reheat when necessary.

2. Determination of Molecular Weight using a Gas Balance (from Kinttof)

The gas balance is filled with dry air and set at 28.8. Dried propylene (30 cm long CaCl₂ tube) is then led out of the gas-holder into the balance. which will be free from air when about 3/4 litre of gas has been passed through. The balance reading gives a molecular weight of 43 (calc. 42.1).

3. Determination of the number of carbon atoms in the propylene molecule by quantitative combustion over copper oxide.

The apparatus consists of a 100ml gas syringe connected to a quartz tube 20cm long and 7mm internal diameter by means of a capillary three-way cock. A layer of copper oxide filings 10.5cm long is kept in place in the tube by means of asbestos wool. Two empty wash-bottles are connected up in the usual way to prevent the carbon dioxide formed in the combustion from passing into the gas burette which is filled with water as a sealing liquid. (If a rubber tube is used to connect the quartz tube to the burette it will not be big enough to cater for the approximately 90ml of carbon dioxide which is formed. Thus most of the carbon dioxide passes into the gas burette and quite noticeable quantities will dissolve in the water and the measured volume will be too small.).

Description of the experiment

The gas syringe is first filled with exactly 30ml of dry propylene Then the cock is closed and, with the through the three-way cock. levels in the burette equalised, a reading is taken which should be close to zero before heating. The quartz tube containing the copper Oxide is now heated with two burners (batswing and a bunsen) until the tube begins to glow red. Because of the heat the volume of the gas increases and the gas passes into the burette where a reading is taken before the cock is opened. After opening the three-way cock the piston is slowly pushed towards the quartz tube. Immediately the volume of gas in the burette begins to increase. By lowering the levelling Vessel every now and then a slightly diminished pressure can be maintained throughout the apparatus. In this way the whole volume of propylene (30ml) is pushed into the quartz tube in small portions each about 1mm in length until, in about 7-8 minutes the piston has reached its furthest point. The three-way cock is now closed. Shortly afterwards the volume in the gas burette reaches its greatest Value and the level is read. The gaseous water formed in the Combustion condenses completely forming a few large drops at the end of the combustion tube. The tube is cooled in about five minutes using wet filter paper and a final reading of the gas burette is taken.

The time taken for combustion and preparing and filling the quartz tube with propylene is about 30 minutes.

Burette Reading

(a) before heating	3.2 ml
(b) "opening cock	8.7 ml
(c) after combustion	100.0 ml
(d) end of experiment	92.7 ml

Volume increase

(a) worked out from (a) and (d) above (cold result) end:

92.7 ml

beginning:

 $3.2 \, \mathrm{ml}$

difference:

89.5 ml

(b) worked out from (b) and (c) above (hot result)

end:

100.0 ml

beginning:

8.7 ml

difference

91.3 ml

The calculated final volume: 90 ml.

As can be seen, both results agree fairly well with one another. Similar reults can be achieved with surprising accuracy when the experiment is repeated several times keeping to the above conditions. If the combustion is too prolonged then both results are high. result (a) is the 'cold' result and it is always smaller than (b), the 'hot' result. This probably arises from the fact that during cooling a small quantity of carbon dioxide passes over into the burette and dissolves in the water . Incidentally similar good results can be obtained for the combustion of propane.

4. Testing the unsaturated nature of the Propylene.

(a) with bromine water.

Even very red-yellowish bromine water loses its colour very quickly when shaken in the closed test-tubes. Bromine water can be added to the propylene several times all according to the size of the tubes. Incidentally a few drops of pure bromine react very well too.

(b) Baeyer Test

Rapid precipitation of manganese dioxide can be achieved using an alkaline solution of potassium permanganate. Otherwise the same as in (a) .

Preparative Addition Reactions.

(a) Rapid preparation of 1.2 dibromopropane

A litre flask (in our experiment it held exactly 1170ml) is filled with pure propylene. This quantity of propylene is calculated to react with 8.35 g or 2.62ml of pure bromine. A noticeable decrease in pressure is observed after the bromine has been carefully added from a pipette with a very narrow jet and after the flask has been closed and gently shaken. After shaking vigorously for about 40 seconds decolourisation occurs and the smell of bromine disappears. The walls of the flask are covered with large quantities of an oily liquid. Most of this heavy oil can be washed out into a separating funnel using three quantities of water, one of 20ml and two of 15ml. The clear 1.2 dibromopropane separates and can be removed. The oil is dried by standing for one day over calcium chloride. Yield 5.5 - 6ml.

(b) Preparation of 1.2 dichloropropane

The experiment is carried out as described in (ref. 6, 224). The action of chlorine is much slowee than that of bromine and so is really only suitable for two-hour practicals. The yield is much smaller than the theoretical.

Conclusion Up till now ethylene has been used to demonstrate the properties of unsaturated hydrocarbons. Propylene, however, has many advantages. It can be prepared very quickly giving a purer product without any sode reactions and at a much lower temperature. The reactivity of propylene is much greater so that quantitative addition reactions can be earried out by the teacher in a short time. The Simplicity and safety of all the experiments make propylene an ideal hydrocarbon for use in practical work carried out by the students themselves.

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INTRODUCING BIOCHEMICAL PROBLEMS

INTO SCHOOL CHEMISTRY

by K. Müntz

The annual uptake of carbon by living things is about 15 x 10 10 tonnes. The mining industry accounts for the re-utilization of only 10 tonnes per year so that industrial use of carbon is only one hundred and fiftieth of the annual turnover. In spite of this remarkably large rate of production of organic material, about 40 million people die each year from starvation. Although this may be largely the result of socio-political relationships, we must not lose sight of the fact of socio-political relationships, we must not lose sight of the fact that this is the most important problem for the human race. The following are possible solutions:- increasing the yield of domestic crops and animals, production of new organisms and foodstuffs by crops and animals, production of new organisms and foodstuffs by synthetic means, in which we include the imitation of natural processes. In each case the new science of biochemistry will play a leading role. It seems reasonable, when one considers all aspects of the problem, that biochemistry and the chemistry of metabolic processes should be included in school curricula.

Biochemistry is on the borderline between biology and chemistry.

It is concerned with the isolation and characterisation of natural products, and with the chemical reactions underlying metabolic processes. Natural product chemistry is the source of many stimulating processes. Natural product chemistry is the source of many stimulating processes. Natural product chemistry is the source of many stimulating processes. Natural product chemistry is the source of many stimulating processes for the chemical and pharmaceutical industries. Medicine, ideas for the chemical and pharmaceutical influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agriculture, farming and industry are all influenced by the results of agricul

Alterations in the content of the syllabus are necessary from time to time in every subject. This is always associated with the danger that the course may become overloaded, and the introduction of new that the course may become overloaded, and the introduction of new subjects must be done at the expense of other material. Consequently subjects must be done at the expense of other material. Consequently subjects must be done at the expense of other material. The author syllabus rearrangement is required. It is always worth considering syllabus rearrangement is required. The author whether the new requirements can be met in other ways. The author believes that biochemistry can be emphasized without serious alterations to the syllabus. Many biochemical problems can be highlighted

The chemist must learn about chemical processes in organisms in order to introduce biological aspects into his teaching. Conversely, the biology teacher must know enough chemistry to be able to consider biochemical problems in class. Closer cooperation between these two scientific disciplines must begin with the planning of timetables and the writing of textbooks. It must be carried further in schools by the redistribution of subject matter where appropriate. The journals read by chemistry and biology teachers must keep them up to date with the latest developments in biochemistry and the chemistry of metabolic processes.

With or without administrative changes along these lines, the re-thinking process must begin with the teacher. The following sections give examples of possible ways in which teachers can introduce biochemistry into the biology syllabus.

BIOLOGICAL ASPECTS OF OXIDATION AND REDUCTION

Oxidation and reduction are first dealt with in the 7th class. Oxidation is presented as an energy-producing process of combustion. The combustion of coal is discussed. Man uses the heat of combustion for his own purposes. In connection with the use of oxygen in artificial respiration children learn that breathing is part of an energy-producing process.

In fact, biochemical oxidation is far more important than industrial oxidation processes. In biological processes more than 100 times as much material is oxidised than in industrial processes. Oxidation of biological material is a necessary condition for the existence of life on this earth.

Biological oxidation produces the energy for all bodily processes, and not only for muscular work as is stated in the textbook for Class 7. In industry, heat energy is used primarily to perform mechanical work. In living organisms oxidation occurs without much evolution of heat and the organism makes use of this process not only to perform mechanical work but also for all movement, reactions to stimuli, reproduction and many metabolic processes. Biological oxidation through breathing and enzyme reactions is the universal source of energy for all processes in living things on the earth and is therefore the source of all human life on earth.

In biological oxidation processes organic compounds are broken down into carbon dioxide, water and ammonia. These substances are dispersed into the atmosphere, partly as gases. This is particularly important for the carbon cycle, since the carbon dioxide concentration in the air is so small that the process of assimilation by green plants would use it all up in a few hundred years. Life on earth is thus based on material cycles, particularly the carbon cycle. In this cycle biological oxidation plays just as important and essential a role as the inverse process of photosynthesis. These examples serve to illustrate the dangers that exist of giving pupils too narrow a view of the significance of oxidation if we fail to mention biological oxidation in chemistry lessons. It is not a question of anticipating biology lessons or of pre-empting material from the biology course, but simply a question of presenting a correct picture of the significance and extent of oxidation processes. The energy released in biological Oxidations must have been stored up in the reactants in accordance with the first law of thermodynamics. This has occurred in nature in a reduction process, which is the fixation of carbon dioxide by photosynthesis in chemical systems. Neither in textbooks nor in syllabuses is any indication given that photosynthesis is the most important reduction process on the earth.

Since reduction is the reverse of oxidation it generally proceeds with absorption of energy. The source of this energy in the photosynthetic reduction of carbon dioxide is sunlight. By this means water is reduction of carbon dioxide is sunlight. It is easy to show pupils then used in the reduction of carbon dioxide. It is easy to show pupils that photosynthesis is a reduction process. Comparison of the formula that photosynthesis is a reduction process. (CH₂O)_n, shows that of carbon dioxide with that of carbohydrates, (CH₂O)_n, shows that of carbon dioxide with that of carbohydrates, in the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecule. Two of these go into the carbohydrate and two dioxide molecules. Two of these go into the carbohydrate and two dioxide molecules.

The burning of cool or mineral oil releases energy which has been stored by plants by the process of carbon dioxide reduction hundreds of millions of years ago. The extreme importance of this reduction of millions of years ago. The extreme in a chemistry course.

Process certainly justifies its mention in a chemistry course.

Reduction and oxidation, and the uptake and release of energy in living organisms, illustrate the validity of physical and chemical laws in relation to biological processes.

BIOLOGICAL VIEWPOINTS IN THE TREATMENT OF CATALYSIS

Catalytic processes play a role in many chemical syntheses and the concept of catalysis and catalytic reactions is treated in school courses. Catalytic reactions are very widespread in ature. Only a few of the metabolic reactions could take place at sufficient speed without catalysis. Organisms contain biological catalysts, the enzymes or ferments. These speed up chemical reactions without altering the position of equilibrium. Biological catalysts are not consumed in the reaction and very small amounts are effective since the catalyst is regenerated when the reaction is over and can be re-used repeatedly. They are basically similar to all other catalysts but they have more far reaching effects than the catalysts used in normal chemistry. They partly regulate the ordered sequence of chemical and physical processes involved in metabolism.

Mention of the extreme importance of catalysis in nature should not be omitted in chemistry teaching.

THE TREATMENT OF OXIDATIVE METABOLISM IN ORGANISMS, AND ITS INTRODUCTION INTO CHEMISTRY LESSONS

Using oxidative metabolism as an example, we now show the importance of dealing with biological problems in chemistry courses. Biological oxidation is dealt with in the 11th class in secondary schools as part of the biology course. The most important problems are covered and corresponding material is found in the textbook for this class. The biochemistry of these processes must be understood by the teacher so that he can present the material clearly to the class.

The main course of biochemical oxidation takes place in steps known as glycolysis, the 3-carbon cycle and final oxidation. We shall now describe these, in more detail than will be possible in class. Finally we shall give a shortened version suitable for presentation to the 11th class. From this will emerge the basic chemistry which pupils must master if their instruction in biology is to be successful.

In glycolysis, see Figure 1, hexoses are degraded to pyruvic acid, during which energy is released in an oxidative step which is preceded by more than ten reactions. In living cells the source carbohydrate is first degraded to monosaccharides. Starches or glycogen (in plants or animals) are degraded to glucose. This occurs as an ester with phosphoric acid, glucose - 1 - phosphate. This is transformed enzymatically by glucose phosphate mutase

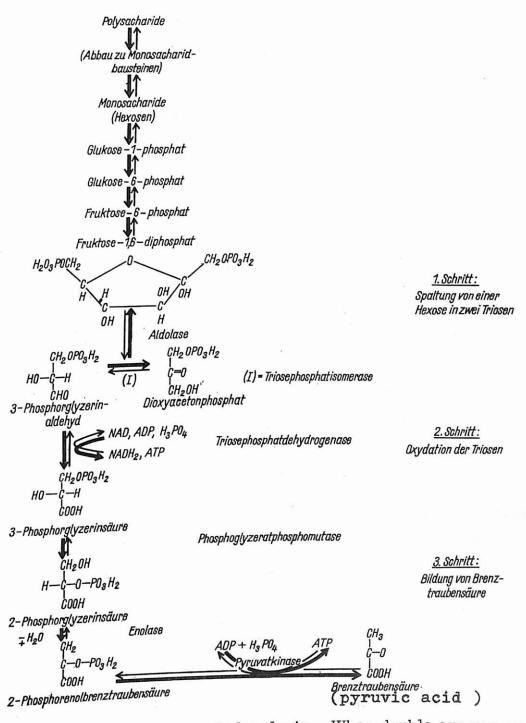


Figure 1: Schematic diagram of glycolysis. When double arrows are given reversible reactions occur. The same enzyme catalyses the reaction in both directions. The thicker arrow indicates the equilibrium position. The equilibrium lies in the direction of the arrow. The catalytic enzymes can be recognised by the ending ...ase .

into glucose - 6 - phosphate. Another enzyme, hexose phosphate isomerase, converts glucos - 6 - phosphate into fructose - 6 phosphate which on further esterification with orthophosphate yields fructose - 1-6 - diphosphate. We then have a double phosphoric ester of a sugar which is degraded by an aldol condensation by the enzyme aldolase into triose phosphate molecules. In this way 3 - phospho-glyceraldehyde and dioxyacetone phosphate are produced, i.e. an aldotriose and a ketotriose. These are in equilibrium with each other, through the agency of an enzyme triosephosphateisomerase, and the equilibrium lies heavily to the ketotriose side. Aldotriose is formed from the ketotriose as the 3 - phosphoglyceraldehyde is used up in further reactions.

The 3 - phosphoglyceraldehyde is consumed in an oxidation reaction to 3 - phosphoglyceric acid. This transformation takes place via at least two steps. The hydrogen formed is taken up by the co-ferment of the hydrogen transfer reaction, nicotinamideadenosine-dinucleotide (abbreviated to NAD). NAD is reduced to NADH, and a phosphate group is taken up by adenosine diphosphate, giving adenosine triphosphate. This compound is the universal energy source and transfer medium in living organisms. The formation of the pyrophosphate linkage between the second and third phosphate residues, and between the first and second requires at least 7000 cals (which is obtained from the oxidative metabolic mechanism).

The 3 - phosphoglyceric acid which is formed is converted enzmatically to 2 - phosphoglyceric acid which is further transformed into 2 - phospho - enol - pyruvic acid by the removal of one water molecule. The phosphate residue in this molecule is then transferred again to adenosine diphosphate (ADP), with breaking of a pyrophosphate link, giving adenosine triphosphate (ATP). As a result of this transphosphorylation pyruvic acid is produced.

The glycolitic degradation of a glucose molecule leads by oxidation to the formation of two molecules of pyruvic acid, two molecules of NADH, and two of ATP.

Pyruvic acid can then react further in a whole series of metabolic reactions. Alanine is formed by amination. Reduction in anaerobic conditions by the reduced NAD from the glycolysis gives lactic acid by lactic acid fermentation. In butyric acid fermentation, two molecules of pyruvic acid give one of butyric acid. Pyruvic acid is decarboxylated in alcoholic fermentation. The products are carbon dioxide (from

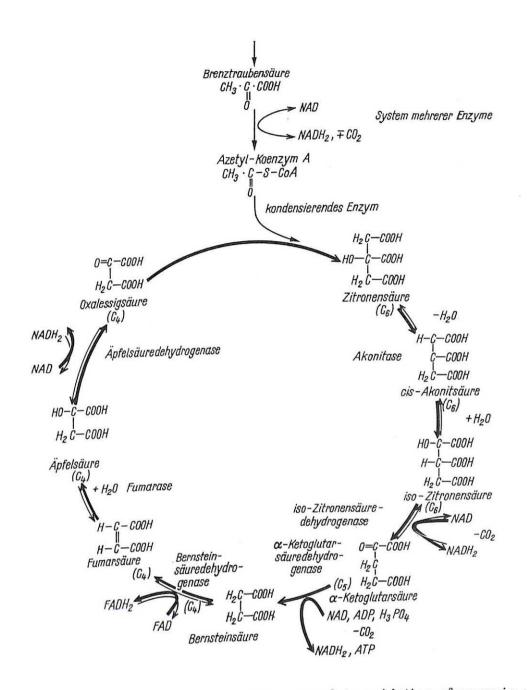


Figure 2. Schematic diagram of the complete oxidation of pyruvic acid. The connection with the glycolytic carbohydrate degradation is made be pyruvic acid; the link with the final oxidation is made by the reduced copyruvic acid; the link with the final oxidation is made by the reduced copyruvic acid; the link with the final oxidation is made by the reduced copyruvic acid; the link with the final oxidation is made by the reduced copyruvic acid in the catalysmes. The diagram has been simplified in the interests of clarity. Coenzyme A is the coenzyme for acylation, i.e. it is involved in the catalysis of transacylation and binds the substrate via a sulphur atom. The sulphur exists as a -SH group in the free enzyme. Coenzyme A is also a nucleotide. The catalyst labelled α -ketoglutaric acid hydrogenase is an enzyme system which somewhat resembles the enzyme for oxidative decarboxylation of pyruvic acid.

the carboxyl group of the acid) and acetaldehyde, which is further reduced to ethanol by ${\rm NADH}_9$ under anaerobic conditions.

In all the reactions of pyruvic acid so far described, a more or less large part of the carbon framework of the hexose, which was the starting material, remains intact. The decomposition or oxidation of the hexose is incomplete. The energy released is correspondingly small. Pyruvic acid can now be oxidised completely, during which all the carbon is released as carbon dioxide and the total available energy (674kcal/mole of hexose) is liberated.

Complete oxidation by the 3 - carbon cycle (Figure 2): This cycle begins with decarboxylation of the pyruvic acid. Simultaneously an oxidation takes place, so that the product is not acetaldehyde but acetyl residues. Two molecules of pyruvic acid (which come from one molecule of hexose) form two CO₂ molecules, two NADH₂ and two acetyl groups. These are not free but are bound to a corresponding

Condensation of one acetyl group with a molecule of oxalacetic acid, which must be 'invested' by the organism, gives one molecule of citric acid. This contains six carbon atoms, two from the acetyl group and four from the oxalacetic acid. In the course of the reactions in the 3 - carbon cycle two carbon atoms from citric acid are completely oxidised to carbon dioxide. The oxidation of the substrate is completed by removal of four hydrogen atoms which re-forms the 'invested' oxalacetic acid with which the sequence can be re-started. Two acetyl groups formed from one molecule of hexose, are converted in the 3 - carbon acid cycle to four molecules of carbon dioxide and eight molecules of hydrogen (most of which is taken up by the NAD).

The single steps are: citric acid is dehydrated to give cis-aconitic acid, which takes up water again to give iso-citric acid (isomerisation). Isocitric acid is decarboxylated and oxidised. The products are CO, NADH, and celetaric acid. This is again oxidised and decarboxylated forming succinic acid, NADH, and CO, Succinic acid is oxidised to fumaric acid and the hydrogen is taken up by a flavin-oxidised to fumaric acid is converted into malic acid by addition of water, which gives oxalacetic acid on oxidation. The hydrogen begin again. The cycle must be completed twice for complete oxidation of a hexose molecule. Apart from the glycolysis reaction and the conversion of pyruvic acid into acetyl residues, the products are six molecules of carbon dioxide, twelve reduced co-enzymes and dehydrogenation and not by atmospheric oxygen.

The hydrogen in the reduced co-enzymes is now oxidised in the so - called 'final oxidation' (or end-oxidation) by atmospheric oxygen. The coenzymes are then again available for reduction during the substrate oxidation step. The oxidation of this hydrogen by atmospheric oxygen is the most important part of biochemical oxidation. This reaction, which is well-known in chemistry as an explosion reaction, takes place step-wise in living cells in redox reactions, with the liberation of part of the energy. These redox reactions are coupled with the energy storage in ATP, which is formed from ADP and inorganic phosphate. Oxidation of the twelve reduced coenzymes gives altogether 34 molecules of ATP and 12 molecules of water. Since 6 water molecules are used up in the course of substrate oxidation, one hexose molecule gives 6 CO2, 6 H2O and 38 ATP . Referred to one mole of glucose, 266kcaf are stored in ATP, i.e. about 40% of the available 674 kcal. The fraction of the total energy stored in the ATP is available for worm, while the remainder must be regarded as lost.

The final oxidation involves nicotinamide, adenosine dinucleotidem flavine and cytochrome. The latter belong to the iron porphyrin group of compounds, which are well-known in connection with haemoglobin. Whereas the reaction between NAD and flavines involves hydrogen, the redox reactions between flavines and cytochromes and between the various cytochromes, take place by electron transfer. As a result the oxidation state of the iron is continually changing. Hydrogen is present as protons, which finally combine with ionised oxygen. The entire final oxidation scheme is shown in Figure 3.

SUMMARY

- 2. Biological oxidation, in contrast to industrial oxidation, takes place without any great heat evolution. The energy released is used to carry out various tasks which are manifested as reproduction, growth, movement and other reflex actions.
- 2. The oxidation takes place by steps in a multi-stage process, catalysed by enzymes. The overall reaction is dehydrogenation of the substrate.
- 3. The hydrogen released is not oxidised by atmospheric oxygen until the final step. In this way some of the energy is stored in phosphate compounds.

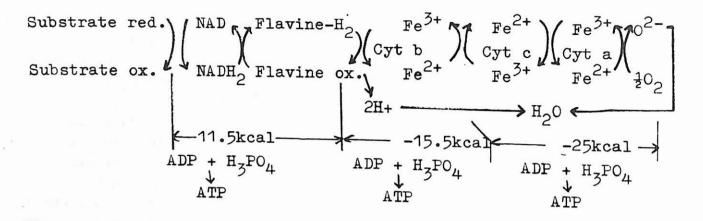


Figure 3. Final oxidation sequence

SIMPLIFIED VERSION FOR TEACHING

Clearly, these metabolic reactions can only be dealt with in a simplified form in class. The simplification should not prevent the pupils from knowing the most important reactions, and obtaining an insight into the true mechanism of biological oxidation. Therefore, the three main stages of oxidative metabolism, namely glycolysis, 3-carbon acid or citric acid cycles and final oxidation should be introduced. The pupils should understand that in living organisms oxidation of the substrate (in particular, glucose) takes place in a series of steps, catalysed by enzymes. In this way hydrogen atoms are split off without the substrate reacting with atmospheric oxygen. The pupils should also understand te final oxidation in principle. The following simplified scheme can be used as a basis:

Glycolysis: Degradation of sugar to pyruvic acid in three stages:

- (a) decomposition of a hexose to two trioses
- (b) the phosphoglyceraldehyde is oxidised to the corresponding carboxylic acid with production of hydrogen
- (c) the phosphoglyceric acid is converted to pyruvic acid. The formal oxidation step is contained in (b).

Acid Cycle: The carboxyl group of the pyruvic acid is split off. Carbon dioxide is formed and oxidation occurs, removing the hydrogen, so that an acetyl residue is formed. This combines with a dicarboxylic acid containing four carbon atoms, forming a six-carbon, tricarboxylic acid (citric acid). By removal of two molecules of carbon dioxide from carboxyl groups and multiple oxidation by removal of hydrogen atoms, citric acid is converted again to the original dicarboxylic acid which was originally present in the cell. original dicarboxylic acid which was originally present in the cell. Simultaneously the acetyl group is completely oxidised to carbon dioxide and water, and in the final oxidation the hydrogen is dioxide and water, and in the final oxidation the hydrogen is 'burned off' with atmospheric oxygen to give water.

Final Oxidation: Whereas in inorganic chemistry the combination of hydrogen and oxygen occurs explosively, living cells have a mechanism for the stepwise liberation of this energy. The single mergy-releasing stages are coupled to other reactions in which energy is stored, so that it remains available to the cell for other functions.

Prerequisite Knowledge of Chemistry: The different forms of oxidation and reduction reactions are already known to the pupils from their chemistry lessons. They also know these processes in relation to the oxidation of alkanes to aldehydes and fatty acids and the converse reduction reactions. They are familiar with the use of catalysts. They know something about the carboxyl group and fatty acids and carbohydrates. They probably hear nothing about the importance of these compounds in living systems and of their properties in these situations in their chemistry lessons. This is left to the biology teacher. It is, however, necessary that the biological function should be pointed out when the corresponding compounds, functional groups or properties are first met in chemistry lessons.

CONCLUSION

Organic nature is the biggest 'chemical factory' on earth. It produces most of the substances needed for direct human nourishment or as raw materials for industry. Since we often allow industrial considerations to influence the way in which chemistry is taught, we ought certainly to avoid omitting the chemistry of living organisms, as has been widely done in the past.

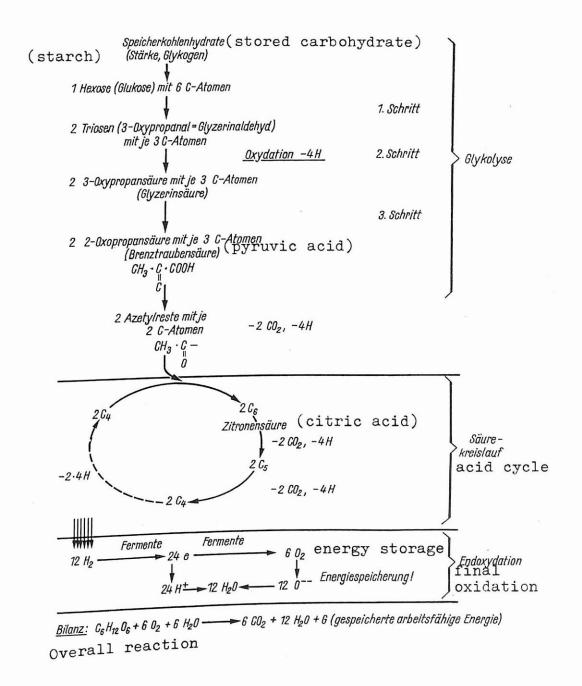


Figure 4. Simplified schematic diagram of the complete oxidation of carbohydrates. Because of the simplification it is not possible to indicate the source of the 6 water molecules on the left of the overall equation. The pupils must be told that six water molecules are used up in the various reactions comprising the complete oxidation of a hexose, so that the set number of water molecules formed during metabolic oxidation in the way shown here is six. This corresponds to the old overall reaction equation given for the process of breathing.

BUILDING MACROMOLECULES

by F. Danusso

(A lecture given at the 2nd Summer School held jointly with the 6th C.E.C.E.C. Congress, Milan, Italy, September 1966)

Introduction "Building macromolecules" is a colloquialism which means: to carry out macromolecular syntheses.

It is well known that macromolecular syntheses are the basic operation of the processes that supply Man with extremely useful materials, which go under the current name of plastics, rubber, fibres, films.

These materials are used for large constructions, such as buildings, tanks, piping, and for a variety of small constructions in a wide sense, such as parts of machines, tools, and small personal and domestic articles of common and widespread use.

For this all "macromolecular materials" (also called "organic materials" in that they are mainly prepared with the substances and methods of organic chemistry) have an exceptionally increasing application. World production is today at the level of several million tons per year and constitutes the economic foundation of many commercial companies.

It is equally well known that macromolecular syntheses are also the basic operations of many biological processes and therefore are involved in the existence of ourselves and of all beings in the animal and vegetable kingdoms. They are, in particular, integral factors in the origin of life.

The reason for this appears to be found on the one hand in the necessity of Nature of "building" living bodies by materials which are able to give them a due consistency, functionality and resistance, and at the same time adaptability to all the stresses of the environment in which their activity must be developed. On the other hand, macromolecular

syntheses satisfy also the requirement, characteristic of Nature, to create a great variety of individuals, collected in a great variety of groups, each gathering elements which are strictly similar, but also distinguishable from each other.

Finally we recall that macromolecular syntheses are able to provide us with ingredients which are valuable for a number of technical, biological and pharmacological applications, in which macromolecular products play the role of chemicals, endowed with peculiar molecular properties associated with specific chemical functions.

The macromolecular syntheses Our present ways of "building macromolecules" are mostly oriented to obtain products of technical interest, and only in small part of biological or pharmaceutical interest.

Our present methods are fundamentally of two types. The first type is the synthesis of macromolecules starting with compounds consisting of small molecules (called a polymerization reaction). The second type is the synthesis of macromolecules starting with a compound, natural or synthetic, synthesis of macromolecules starting with a compound, natural or synthetic, already macromolecular (called a modification reaction).

The first type of macromolecular synthesis is of greater interest for our present economy and we will presently return to it.

The second type has been prominent in the past, beginning during the second part of the XIX Century, and is typical of the industry of transformation of natural products, as, e.g., the cellulose industry. It is seldom used in the industry of the fully synthetic products, or it is used only for a in the industry of the fully synthetic products. secondary, partial modification of more conventional products.

An example is the following modification reaction typical of the cellulose industry, by which pure cellulose is transformed in cellulose nitrate by an esterification reaction with nitric acid:

The reaction is illustrated for a repeating unit of the cellulose containing three alcoholic groups, and for a complete esterification reaction. The same reaction could of course be partially carried out, yielding cellulose mononitrate or dinitrate, instead of cellulose trinitrate.

Another typical example is the modification reaction which can be carried out on the side groups of polyvinylacetate, that is of a synthetic polymer, (two units are indicated in this case):

It is an alcoholysis reaction, in which the starting polymer is converted into polyvinylalcohol. The interest of this reaction is to be found in the fact that it is impossible to prepare polyvinylalcohol by polymerization of monomeric vinyl alcohol, because this last compound is unknown and would be unstable in any practical reaction condition. On the other hand,

polyvinyl alcohol is a very interesting ingredient or material for application, so that it is economically convenient to synthesize first polyvinylacetate by polymerization and then convert this polymer into polyvinylalcohol.

A further example of modification reaction is that by which polystyrene is sulphonated by sulphuric acid in the phenyl side group in a more or less regular manner, thus yielding a polysulphonic acid:

$$\begin{array}{c} \text{CH}_2 \\ \text{CH} \\ \text{CH}_2 \\ \text$$

This reaction is especially useful for the preparation of ion exchange resins, of the cationic type, by modifying polystyrene chains belonging to beads of cross-linked polymer.

In spite of the practical importance in many instances of the modification reactions, the most interesting macromolecular syntheses at the present time are the polymerization reactions. These permit us to produce macromolecular substances starting from suitable substances of small molecule, called substances starting from suitable substances as the products of the processes of the "monomers", available in large quantities as the products of the processes of the present heavy organic chemistry industry.

In this case the macromolecule can be synthesized by joining together a great number of molecules of the monomer in an "addition" reaction.

Alternatively the macromolecule can be synthesized by binding together the essential parts of the monomer molecules, with the simultaneous elimination of a by-product of smaller molecule - i.e. a "condensation" reaction.

In both cases the small molecules of the monomer (or essential parts of

them) are joined together by covalent, or nearly covalent, bonds, so that they give rise to a repetitive structure essentially constituted by the linkage of numerous "repeating units". This is the reason why the macromolecular products are usually called "polymers", in that their molecules are composed by "numerous parts", according to the etymology of the term.

In other words, having a macromolecule a size of hundred, thousand, ten thousand and even more times the size of a common molecule of the organic chemistry, we are unable in practice to build it step by step, at least in a reasonable time. We must on the contrary proceed by joining together statistically, by a single but complex reaction, many small pieces, which are equal or belong to a very few types ("monomeric units").

Thus, the "construction" of a macromolecule proceeds for us in a way completely analogous to that of the construction of a building. For this, in fact, we must join together many relatively small elements, such as bricks, stones, beams and pillars, proceeding by a number of small steps of an essentially repetitive character.

By a polymerization reaction suitably carried out with a mixture of monomers, instead of only one monomer, it is possible to synthesize macromolecules consisting of as many types of units as the number of monomers in the mixture (usually two, seldom three or four). In this case the product is more correctly called "copolymer".

The "molecular" nature of the polymers — This brief outline permits us to account for the great variety of properties of macromolecular materials and for the possibility of including in them materials which canbe stiff or highly elastic, brittle and glassy or tough, hard or soft, amorphous or crystalline. Their macroscopic properties intimately depend on the structure of their constituting molecules, a structure which can be chosen in a practically infinite number of ways.

We recall here that an important step in macromolecular syntheses is the formation of covalent or nearly covalent bonds.

In fact our traditional aim is to create structures which first of all are "molecular", that is structures consisting of molecular species in whatever (non-destructive) conditions they can happen to be. Covalent bonds are sufficient condition in order to obtain a "molecular compound".

If, e.g., the bonds between units were of an ionic character, then in a polar medium the probable corresponding macromolecule could undergo a kind of degradation process and transform into ionic species, which in the limit would be monomeric, and no longer polymeric. Thus, a number of chemical compounds have to be excluded from the field of macromolecular chemistry, and to be left to other disciplines of chemistry. A macromolecule can be synthesized on the basis of bonds different from the covalent or nearly covalent only if a particular structure is found which imparts sufficient stability to the main chain.

A typical example is that of silica, studied by inorganic chemistry, which practically cannot exist in a molecular form as ${\rm SiO}_2$. As a matter of fact a practically cannot exist in a molecular form as ${\rm SiO}_2$. As a matter of fact a silica single crystal could be thought of as a single cross-linked macromolecule, with a tetravalent ${\rm SiO}_2$, repeating unit, as it may be represented by the following scheme:

The bonds between units are in this case partially covalent and partially ionic. It is well known that silica can be transformed into acidic monomeric or possibly oligomeric ionic species when dissolved in a polar medium, e.g. water, and it acquires quite different properties. On the other hand, silica is a glassy, stiff material useful mainly in combinations other hand, silica is a glassy, stiff material useful mainly in combinations other materials or compounds.

In order to obtain really macromolecular substances in some way based on the silica structure, we have to synthesize polymers, called "silicon on the silica structure, we have to synthesize polymers of inorganic - SiO - polymers". In these the linear main chain does consist of inorganic - SiO - polymers". In these the linear main chain does consist of inorganic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, but lateral organic substituents R units, like single linear chains of silica, like si

oxygen of e.g., a polar kind.

The resulting polymers are very stable in many different conditions and are very useful in a number of applications, with a processability completely different from that of silica.

As a matter of fact, a great number of inorganic compounds are not truly molecular and in the crystalline state have a structure which could be classified as macromolecular, but only in that particular condition.

As a limiting example of this statement, we can think of sodium chloride, in which the bonds are of a fully heteropolar character. A single crystal of this has a uniform pseudo-macromolecular structure, but when dissolved, for instance in water, it is completely dissociated into ions of atomic size. In this respect, a single crystal of sodium chloride can be conceived as a "store" of very small ions, but not a molecule. By dissolving sodium chloride in non-polar solvents, a dispersion can be obtained of oligomeric or probably also monomeric molecules, with properties again quite different from those of sodium chloride in crystal state or dissolved in polar media.

It is therefore clear that we cannot envisage a macromolecular substance consisting of sodium and chlorine.

In this connection we recall that, by methods of macromolecular chemistry, a new class of polymers has been synthesized in recent years and presented under the name of "inorganic polymers". The above mentioned silicon polymers are a typical example of inorganic polymers, because the backbone of their macromolecules has a structure not belonging to organic chemistry. The side groups must be, however, of an organic kind. In the light of the above discussion about inorganic compounds it appears to be preferable to use for these polymers the term "elementorganic polymers", already introduced by several scientists, instead of that of "inorganic polymers".

Macromolecular structures can, however, be easily obtained by chain

formations which are typical of organic chemistry. The following examples can be given:

Polyvinyl chain:

Polyether chain:

Polyamide chain:

Polyester chain:

Polycarbonate chain:

Cellulose chain:

It may be seen that the main chain may consist of carbon atoms only, as in polyvinyl chains, but may also contain elements or groups different from carbon, e.g.- polyether chains, which contain oxygen atoms; polyamide chains, with nitrogen and amide links; polyester chains, containing oxygen and ester links; polycarbonate chains, with oxygen in carbonic acid residues; cellulose chains, having cyclic structures, with oxygen of ether type in the cycles and other side groups of primary and secondary alcoholic type; and so on.

These examples refer to linear chains. For branched or cross linked macromolecules the considerations can be more complicated, but the basic concepts are exactly the same. This is the reason why in the outline which will follow we will mention for simplicity only linear chain structures and will neglect to extend our consideration to branched or cross-linked polymers.

Principles for polyreactions It is now interesting to examine polymerization reactions starting from general concepts of chemistry, that is to examine the principles of a unitary theory of polymerization.

University courses usually present systematic descriptions of examples of different groups of polymerizations, but seldom attempt to present the topic in a single scheme. We will attempt here to proceed in a converse way, by considering first the possible principles, and then showing, in the available space, some examples having a special meaning.

When we pay particular attention to the characteristic features which are common to polymerizations of any type we (and Nature) can utilize, we realize that they follow one basic principle, that we can explain in the following terms.

Polymerizations take place, as we have seen, not by a simultaneous combination of a great number of monomer molecules, but through a great number of repetitions of a single reaction.

This reaction cannot obviously be monomolecular; it will be at least bimolecular, in that we want as a result an increase in the molecular size of the product. Incidentally, it could be perhaps termolecular, but we know that this occurrence is very infrequent.

With these preliminary remarks, it is clear that the synthesis of a macromolecule will take place only if the product (or at least one of the products) of each event of reaction is able to be reagent in a second event of the same reaction, and to transfer itself (part or all) into the active product of the second event of the reaction.

An example is that of the esterification reaction applied to a suitable oxy-acid to give a poly-ester chain:

$$-H_2O$$
 \longrightarrow HO-R-COOH + HO-R-COOH
 \longrightarrow HO-R-COO-R-COOH
 \longrightarrow HO-R-COO-R-COOH
 \longrightarrow HO-R-COO-R-COOH

The whole reaction becomes a "polyreaction" only when this principle is obeyed, that is a reaction which has the desired repetitive and cumulative character, and which gives rise to the linkage of small molecules into big molecules.

Reagents suitable for polyreaction Two questions immediately arise.

The first one: What reactions are able to give rise to a polyreaction? The second one: What reagents are suitable for the development of a polyreaction?

The two questions are in fact interdependent, because a selected reaction is suitable if a convenient reagent is also found, and, conversely, a selected is suitable if a convenient reaction. Substance can be a monomer only if it is able to follow a convenient reaction.

On a purely theoretical ground one should answer both the questions by resolving the following points:

- 1 Choose a substance as formal monomer.
- 2 Make the list of the possible, bi- and polyvalent units that can be stoichiometrically derived from that substance.
- 3 Select the units which can be bound together by covalent or nearly covalent bonds (or in any case by stable bonds).
- 4 Choose one of these units.
- 5 Find a reaction suitable for transforming the chosen monomer into that unit in such a manner that this last can be added to other equal units.
- 6 Compare the result with those derived from other monomers which can give rise to the same unit (and therefore to the same polymer).

The evaluation of the whole situation is of course very complex: first because points 3 and 5 are not completely solved by the present methods of theoretical chemistry; and secondly because point 6 should comprise all the relationships between monomers established by normal reactions of organic chemistry, in that each monomer could in general be prepared from other monomers. In this respect the solution should be also optimized.

In order to clarify this matter, it is interesting briefly to discuss an example for the simple case of polymethylene chains.

From the purely chemical point of view, we could think of methane as the simplest formal monomer. It has the stoichiometric possibility to give rise to three structural units, bi-, ter- and tetravalent:

the bonds between such units can be covalent bonds and in fact we know today polymers or copolymers consisting of these three units. Actually the first one we find in linear polymethylene or polyethylene; the second one we can recognize as a co-unit in branched or cross-linked polyethylenes and the third one is the base unit of the diamond, which is formally a cross-linked polymer, because in its crystals the carbon atoms are bound by covalent bonds.

In this way, methane could be theoretically an interesting monomer, but in practice we do not know at present a polyreaction able to transform it into any polymer.

On the other hand, the same unit -CH₂-, or units multiple of it, can be derived from other compounds, and in fact we are able to synthesize polymethylene chains by at least three different monomers, as in the following reactions:

1)
$$CH_2 = CH_2$$
 (ethylene)

2) $CH_2 = CH_2$ (polyethylene)

2) $CH_2 = CH_2$ (polymethylene)

3) $CO + 2H_2$ (polymethylene)

(Fischer mixture)

The first one is the formation of polyethylene units in the polymerization of ethylene for which more than one polyreaction is known; the second one is the formation of polymethylene units from diazomethane, by one is the formation of polymethylene units from carbon dioxide and the third one decomposition of this compound and release of nitrogen; and the third one is the formation of polymethylene units from carbon dioxide and hydrogen is the formation of polymethylene units from carbon dioxide and hydrogen in the Fischer's synthesis of linear paraffins.

It is apparent that these three monomers can all be derived from methane (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich in natural (which occurs in the chemical industry of certain countries rich industry

From this discussion it is interesting to conclude that in principle almost any substance could be a monomer, but that the number of real monomers is largely limited by our knowledge of reactions, or reaction conditions, which can develop a polyreaction.

In this connection we must also remember that, following this definition

of monomer, in many polymerizations we know today the real monomer is not the substance we introduce as reagent, but is a different chemical species which forms in the reaction system. We will presently see some examples of this type of polymerization.

Basic reactions suitable for a polyreaction The types of reaction that at the present time are used to develop a polyreaction can be classified into two categories: condensation reactions and addition reactions.

The principal types of these reactions can be symbolically represented as follows:

Condensation

Addition

3)
$$A + A \longrightarrow A_2$$
 (equal reagents)

A condensation reaction is one in which a by-product is released and the principal product results from the combination of the essential parts of the two reagent molecules.

Organic chemistry does not consider usually this reaction as a type apart, but defines many reactions which fall under our wider definition. These are, e.g., esterification reactions, amidation reactions, etherification reactions, Wurtz reactions, Schotten-Baumann reactions and so on.

An addition reaction is, on the contrary, a general type of reaction, considered also by organic chemistry, in which only one molecule is produced

as stoichiometric sum of two reagent molecules. The two reagent molecules can be, or not be, equal. If they are not equal, the combination can occur either as juxtaposition of the two molecules (reaction 4), or by insertion of one molecule into the other (reaction 5), followed in both cases by rearrangement of their electronic configurations. In the second case (reaction 5) the reaction is also called "telomerization", because the inserted molecule M acquires two end groups, that are the two portions, A and B, into which the other molecule has been split.

A polyreaction on the basis of a condensation or of an addition reaction, can be respectively called a "polycondensation" or a "polyaddition".

It is interesting to note that this distinction, which seems to be very clear and absolute, can meet intermediate cases that are in some way difficult to classify, or whose classification appears to be somewhat arbitrary.

Let us consider, e.g., the reaction by which phenol and formaldehyde give macromolecular products. Even if complicated, it can be essentially presented as follows:

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We may see that, for the formation of two successive bonds of the chain two different reactions are necessary. The first one is without ambiguities an addition reaction, which forms an intermediate alcoholic terminal group; the second one is clearly a condensation reaction which eliminates water and forms the methylene bridge between phenol units. For different reasons the whole reaction is traditionally considered a polycondensation, mainly because of the mechanism of reaction and of the elimination of water. As a matter of fact the real monomer of this polyreaction can be seen in the phenol-alcohol (indicated at the foot of the diagram) whose synthesis is brought about by virtue of the addition step of the reaction.

Thus, in this case the polyreaction can be correctly regarded as a polycondensation, with the reservation that phenol and formaldehyde are only suitable reagents for the formation of the real monomer in the reaction system itself.

Essentially the same diagram can be used for attributing to polycondensation also the reaction between urea and formaldehyde, which is known to yield linear or cross-linked polymers.

Another interesting polyreaction of special kind is that which can be called "polycombination", an example of which is as follows:

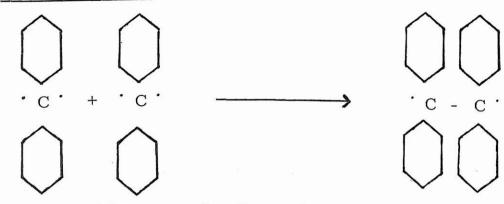
Diphenylmethane can be attacked by a suitable radical R' (e.g. a peroxide radical) to give a diphenylmethyl radical. This last can combine with a similar radical to give an inactive intermediate product, which can be again attacked by another auxiliary radical R' to give, first, a new, oligomeric, and then a polymeric radical, which, in its turn, combines with a similar radical. By repeated combination of radicals one can reach, in suitable conditions, high molecular weights in the product.

It is difficult to identify this polyreaction as a polycondensation rather than a polyaddition. The following two reaction schemes can be suggested:

(R = a by-product carrier)

Condensation Scheme

Addition scheme



(R = a reagent for preparing the real monomer)

The first process is of condensation; the second one of addition. However, the condensation alternative is of an unusual kind, and the addition scheme is applied to a radicalic species which could not be strictly considered as a monomer.

Another polyreaction of ambiguous attribution is the poly-imide formation starting with suitable bifunctional monomers, containing anhydride and amine groups:

The first step of reaction is an addition which forms an amide link; the second step transforms the active functional groups into a more stable imide group. This reaction is today considered very interesting for the preparation of high temperature resistant polymers.

Here, from the point of view of the macromolecular synthesis, the first step of reaction may appear to be the most important, being strictly sufficient for the formation of macromolecules; the second step could be regarded as a modification reaction, so that the polyreaction could be identified with a polyaddition. On the other hand, only the second step of reaction gives to the polymer the stable structure and all the properties we expect from a polymer built up with double imide links, and we might have good reasons to call the whole process a polycondensation.

Another interesting type of complication is the coupling of the basic reaction with another unessential reaction. An example is a polyreaction called "cyclopolymerization", which applies to suitable non conjugated dienes and can be presented as follows:

$$K' + CH2 = CH - R - CH = CH2$$

$$K - CH2 - CH
$$R$$

$$CH2$$

$$CH3$$

$$CH4$$

$$CH2$$

$$CH2$$

$$CH3$$

$$CH4$$

$$CH2$$

$$CH3$$

$$CH4$$

$$CH4$$

$$CH2$$

$$CH4$$

$$CH4$$$$

$$K-CH_{2}-CH$$

$$CH_{2}-CH$$

$$CH_{3}-CH$$

$$CH_{4}-CH$$

$$CH_{4}-CH$$

$$CH_{5}-CH$$

$$CH_{5}-CH$$

$$CH_{5}-CH$$

$$CH_{6}-CH$$

$$CH_{7}-CH$$

$$CH$$

This reaction can be initiated by the attack of a radical to the monomer. By an addition step, a monomeric radical is formed, keeping the unpaired electron on one of the two double bonds of the monomer. By a second step of reaction, an isomerization takes place, and the second double bond gives rise to a cyclic structure. The cyclic monomeric radical can again attack a monomer molecule and repeat an addition step, followed by isomerization of the new radical, and so on, developing a polyaddition. This type of polyreaction of cyclic structures on the main chain can impart to the polymer a set of properties, such as heat resistance, high melting point, which have useful practical applications.

Complications of the kinds we have mentioned here are relatively unfrequent. In general they arise when the basic reaction is not single, but composed by more than one step, as a rule two steps.

The distinction between polycondensation and polyaddition is sometimes based, by certain scientists also on the chemical or rather kinetic mechanism not only of the basic reaction, but also of the polyreaction itself.

In this connection, it can be useful to present some examples of polycondensation reactions which can be regarded as having an unusual scheme or mechanism of reaction.

The first one is the formation of an polyaminoacid by opening of a carboxy-anhydride ring:

$$X \quad HN - CH - CO \longrightarrow \begin{bmatrix} -NH - CH - CO \end{bmatrix}_{X} + XCO_{2}$$

The reaction eliminates carbon dioxide, but the polyreaction follows a scheme frequently encountered in polyadditions, with an intermediate activated species that could be similar to a kinetic chain carrier. On the other hand, kinetic chain reactions are not considered in general in a conventional kinetic scheme of polycondensation.

The second one is the formation of a polyalkilidene starting from a diazo-alkylidene compound:

Here nitrogen is released as a result of a "decomposition" of the monomer, and not as by-product of a reaction in which two monomer molecules are stoichiometrically concerned. Furthermore the addition of the alkyldenic units takes place by a kinetic chain reaction, in the presence of initiators which are used for typical polyadditions.

Nearly the same remarks could also be applied to the third polyreaction, which would on the contrary appear based on a typical condensation reaction with the formation of polybenzylene:

$$X \longrightarrow CH_2C1 \longrightarrow \begin{bmatrix} & & & \\ & & & \\ & & & \end{bmatrix}_X + X + HC1$$

Reaction scheme of polycondensation We will examine, now, some polyreaction schemes, which can be taken as typical of the great majority of polymerization reactions. We will consider first polycondensations, and then polyadditions, thus following a traditional classification. We will limit ourselves in any case to the formation of linear polymers.

We have understood that polycondensation reactions may be, in principle, carried out with one bifunctional monomer, bearing both the chemical functions, or with two bifunctional monomers, each bearing only one of two types of function. Thus we can in practice distinguish a "one monomer polycondensation" from a "two monomer polycondensation", even if the two polyreactions are essentially the same.

Considering for simplicity only the case of one monomer, the reaction scheme of a typical polycondensation process is the following one:

$$aAb + aAb \xrightarrow{-ab} aA_{2}b$$

$$aA_{2}b + aAb \xrightarrow{-ab} aA_{3}b \qquad aA_{2}b + aA_{2}b \xrightarrow{-ab} aA_{4}b$$

$$aA_{3}b + aAb \xrightarrow{-ab} aA_{4}b \qquad aA_{3}b + aA_{2}b \xrightarrow{-ab} aA_{5}b \qquad aA_{3}b + aA_{3}b \xrightarrow{-ab} aA_{6}b$$

$$aA_{3}b + aA_{5}b \qquad aA_{3}b + aA_{3}b \xrightarrow{-ab} aA_{6}b$$

$$aA_{3}b + aA_{5}b \qquad aA_{3}b + aA_{3}b \xrightarrow{-ab} aA_{6}b$$

$$aA_{3}b + aA_{5}b \qquad aA_{5}b \qquad aA_{5}b$$

$$aA_{5}b \qquad aA_{5}b \qquad aA_{5}b \qquad aA_{5}b$$

$$aA_{6}b \qquad aA_{6}b \qquad aA_{6}b \qquad aA_{6}b$$

Examples of monomers are:

HO ~ COOH (or HO ~ OH + HOCO ~ COOH)

$$H_2N$$
 ~ COOH (or H_2N ~ NH_2 + HOCO ~ COOH)

 H_2N ~ COC1 (or H_2N ~ NH_2 + C1CO ~ COC1)

This can be called a "branching scheme", because the number of possible reactions for any reagent increases by the increase of the extent of reaction and, simultaneously, of the degree of polymerization (that is the molecular

weight of the product). This is because the monomer and every intermediate species can react with itself and with any other species present in the reaction system. The kinetic mechanism of this polyreaction is in general a stepwise mechanism, in the sense that every single event of reaction gives rise to a stable, non activated product, which is nevertheless reactive for a subsequent event of reaction. In other words, every molecule in the system is not particularly activated and can react with any other molecule of the system itself.

In the polyreaction scheme given above, the possible reactions are arranged in such a way that we may see the following: in the first line a molecule of monomer can react with another molecule of monomer, to give a molecule of dimer; in the second line a molecule of dimer can react again with a molecule of monomer to give a trimer, but it can alternatively react with another molecule of tetramer; in the third line a molecule of trimer can react again with a molecule of monomer, or again with a molecule of dimer, or with a molecule of the trimer itself, to give respectively a tetramer, a pentamer, and a hexamer, and so on. The general reaction is also indicated, according to which every molecule can react with any other molecule to give a molecule of product which has, as degree of polymerization, the sum of the degrees of polymerization of the two reagent molecules. As a consequence, the molecular weight of the product increases with the extent of reaction.

In the industrial practice it is easier to meet two monomer polycondensations. Three typical polycondensations are symbolically the following ones:

b) Polyamide (2 monomers: for ex. HOCO-(CH
$$_2$$
) $_4$ -COOH + $_2$ N-(CH $_2$) $_6$ -NH $_2$)

$$-NH_{2} + HOCO-R-COOH + H_{2}N-R'-NH_{2} + HOCO-R-COOH + H_{2}N-R'-NH_{2} + HOCO-R-COOH + H_{2}N-R'-NH-CO-R-CO-NH-R'-NH-$$

The first one is a one monomer polycondensation, which is used to produce a polyamide from an amino-acid; the second one is a two monomer polycondensation, which again produces polyamide from a bicarboxylic acid to produce a polyester from a bicarboxylic acid and a glycol

The three reactions are industrially useful for the production of high molecular weight polymers, which are mostly applied in spinning processes or films.

The branching scheme polyaddition Whereas polycondensations practically follow only one scheme of polyreaction, polyadditions can follow different

When the two functions of the monomer which make the polyaddition

possible are sufficiently independent of each other, the polyaddition can follow an individual reaction scheme quite similar to that of polycondensation:

and in general:

$$\mathbf{M}_{\mathbf{m}} + \mathbf{M}_{\mathbf{n}} \longrightarrow \mathbf{M}_{\mathbf{m}+\mathbf{n}}$$

In this case we will call it a "branching scheme" polyaddition.

As we may see in the reaction scheme, in the first column are the addition reactions in which the monomer only is involved; in the second column are the reactions with the dimer; in the third column the reactions with the trimer, and so on. The general chemical equation expresses the possibility that a molecule of any intermediate stable species can react with a molecule of any other intermediate species, giving a product whose molecular weight is the sum of the molecular weights of the two reagents.

Some examples of monomers are the following ones:

$$R$$
 HN
 $CH=CH_2$
 $CH=CH_2$

For the first one the basic reaction is the addition of a secondary amine group to an activated double bond; for the second monomer the addition is that of a mercaptan group, again on a suitable double bond; for the third monomer the addition takes place between an alcoholic group and an isocyanate group. By side, the couples of monomers are indicated for a corresponding "two monomer polyaddition".

Although very interesting in many respects, the "branching scheme polyaddition" is only seldom applied in practice. A well known industrial process of this type is the synthesis of urethane polymers, which find many very important applications. It is essentially a two monomers application, that uses a monomer mixture of the third type indicated in the examples of monomers.

The linear scheme polyaddition The majority of the present commercial polymers is synthesised by polyadditions, following a more simple scheme, that we will call "linear scheme polyaddition". These polyreactions follow, in principle, only the individual reactions of the first column of the "branching scheme" polyaddition, in that only reactions with the monomer are essentially possible, and not, as a rule, reactions between intermediate species:

In the polyaddition indicated as of the first type in the above scheme, the addition of two monomer molecules gives rise to an activated dimeric species (e.g. a radical), which starts a series of additions of monomer molecules to a growing intermediate species, which keeps the activation of the initial

This scheme has some more frequent variants that rise from the introduction into the system of a foreign substance C, which plays the role

of a catalyst in a true sense or simply of an initiator. In this case the reaction scheme becomes of the second type.

According to the second type of scheme, a foreign substance C yields an activated foreign species C*, which is able to attack a monomer molecule to give an activated monomeric species. This last starts a series of additions of monomer molecules to the growing activated species, as in the scheme of the first type.

In the third type scheme, a foreign substance C can directly attack a monomer molecule giving rise to a monomeric activated species CM^* , which starts the series of monomer additions exactly as in the second type scheme.

The last fourth type scheme is very similar to the third one. It differs in that a particular activation is absent, and the growing intermediate species is practically a molecular species (symbolically indicated without an asterisk).

It is to be noted that, in any case, the foreign substance C can be known and introduced in the system as such, or alternatively it can be unknown, at least in detail, and can be formed in the reaction system by introducing another substance A, or two other substances A and B, which are reagents for its formation.

The monomers suitable for a linear scheme polyaddition are very numerous. It is interesting to remark that, on a purely theoretical ground, it is possible to predict that a suitable monomer must in this case contain the two functions, which make the addition possible, strictly interdependent. In general, functions of this kind are to be sought in ring structures, which can be immediately apparent or, more frequently, generalized. Suitable ring structures can be opened by selecting convenient reaction conditions, giving rise to bivalent units, which can retain the initial activation in the intermediate species and in every stage of the reaction.

In some cases a suitable ring structure can be easily recognised in cyclic substances, but more frequently it reduces to a two membered ring structure, that is to a double bond, whose ring strain can be considered, at least in principle, especially high.

A few examples of monomers are the following ones:

$$CH_2 = CH_2$$
 $CH_2 = CH$ $CH_2 - CH_2$ $H_2C = O$

Turning back to the possible types of linear scheme polyadditions, it can be interesting to remember that the chemical mechanism of reaction of all the four types can be either radical or ionic. In fact, a generalized ring structure can be opened through either a homolytic or a heterolytic breaking of a key bond. This opening can be determined by the attack of a radical, or of an ion, or anyhow by a polarization induced by the electrostatic forces of a convenient bond of the attacking species.

From a kinetic point of view, schemes of the first, second and third type are typical of the so called "chain reactions". The growing intermediate species acts as a chain barrier. On the contrary, the fourth type is essentially that of a stepwise addition, with stable intermediate species, devoid of the character of a kinetic chain.

It is to be noted that the schemes we have indicated are not complete. As a matter of fact the series of reactions can frequently undergo a termination process, which in some way stops the growth of the intermediate species. Thus, chain reaction polyadditions are, as a rule, terminated by a chain termination reaction.

Stepwise polyadditions can include processes equivalent to a chain termination, but in a few cases, incarefully selected experimental conditions, they can be devoid of any termination. Such polyadditions, indefinitely opened to a growing process, can give rise to a system which was given the name of 'living polymer'. This name is derived from the possibility of the system of 'eating' any new amount of monomer which may be added occurred and the system stood without polymerization.

Examples of radical and ionic polyaddition mechanisms — It can be interesting to conclude the topic of the linear polyaddition with an example of a complete set of reactions of the well known radical polymerization:

$$C \longrightarrow a C'$$

$$C' + M \longrightarrow M' (\equiv CM')$$
Initiation

$$M_{2}^{*} + M \longrightarrow M_{2}^{*}$$

$$M_{2}^{*} + M \longrightarrow M_{3}^{*}$$

$$M_{3}^{*} + M \longrightarrow M_{4}^{*}$$

$$M_{1}^{*} + M \longrightarrow M_{1+1}^{*}$$

$$M_{1}^{*} + M \longrightarrow M_{m+1}$$

$$M_{m}^{*} + M_{n}^{*} \longrightarrow M_{m} + M_{n}$$

$$M_{m}^{*} + M \longrightarrow M_{m} + M^{*}$$

$$M_{m}^{*} + S \longrightarrow M_{m} + S$$

We may see that four different stages take place. In the initiation stage, an initiator C yields a certain number of radicals C', which are able to attack a monomer molecule giving rise to a monomeric radical M*, by an addition The radical M* immediately follows the propagation stage, by a reaction. number of very fast additions to monomer molecules. This propagation is sooner or later stopped by two possible termination reactions, consisting of a deactivation of growing radicals by a mutual interaction of the radicals themselves, which concludes with either a combination or a disproportionation Polymer molecules are thus essentially produced as a consequence of the termination stage, but a further type of process can take place. transfer process, which equally yields molecules of polymer before the propagation is terminated. The above scheme reports, as an example of the transfer stage, two typical transfer reactions with a foreign substance S. whose presence can be fortuitous, or sometimes desired, in the system. Transfer reactions with a foreign substance are very important because they are a practical means of reducing the molecular weight of the polymer produced.

Whereas in radical polymerization the presence of individual radicals is quite natural, the existence of individual ions is unnatural. We can therefore assume that ions are effective only through the formation of ionic pairs. These pairs can be more or less dissociated. If they are highly dissociated the two individual ions can act almost as individual entities, and behave like the so called "free ions" of organic chemistry. If the ionic couples are, on the contrary, only slightly dissociated, their behaviour is in the limit, like that of weakly polarized bonds, in which the electrical charges are only scarcely separated.

Some schemes of ionic initiation processes can be the following ones, followed by corresponding real examples:

Ionic Initiation processes

a)
$$C + M \longrightarrow C^{(-)}M^{(+)}$$
 (cationic)

b)
$$C + M \longrightarrow C^{(+)}M^{(-)}$$
 (anionic)

c)
$$A + B \longrightarrow AB \longrightarrow A^{(-)}B^{(+)}$$

 $A^{(-)}B^{(+)} + M \longrightarrow C^{(-)}M^{(+)}$ (cationic)

d)
$$A + B \longrightarrow AB \longrightarrow A^{(+)}B^{(-)}$$

 $A^{(+)}B^{(-)} + M \longrightarrow C^{(+)}M^{(-)}$ (anionic)

Examples:

a)
$$HX + CH_2 = CH \longrightarrow CH_3 - CH X (-)$$

b) MeH +
$$CH_2 = CH \longrightarrow CH_3 - CH Me$$
 (+)

c)
$$BF_3 + H_2O \longrightarrow BF_3$$
 $H_2O \Longrightarrow \left[BF_3OH\right]^{(-)}H^{(+)}$

$$\left[BF_3OH\right]^{(-)}H^{(+)} + CH_2 = CH \longrightarrow CH_3 - CH \left[BF_3OH\right]^{(-)}$$

d) Na + NH₃
$$\xrightarrow{-H}$$
 NaNH₂ $\xrightarrow{-H}$ Na(+)NH₂(-)

Na(+)NH₂(-) + CH₂ = CH $\xrightarrow{-H_2}$ H₂N-CH₂- $\overset{\leftarrow}{CH}$ Na(+)

Schemes a) and b) show the formation of an anion pair by interaction of the monomer with an initiator or catalyst C.

In general the ion pair formed can be of two types, depending on the polarity assumed by the monomeric part of the pair. We will assume that the polymerization can be said "cationic" when the monomeric part takes the positive charge, and "anionic" when the monomeric part takes the negative charge. Furthermore, we will call "counterion" the pole of the pair not belonging to the monomeric part, that is the counterpartner of the ion which will undergo the growth process.

The first two examples relate to the formation respectively of a cationic pair and an anionic pair, the first one by the attack of a proton acid to a conveniently substituted vinyl double bond, the second one by the attack of a metal hydride. The counterions are indicated in square brackets.

Schemes c) and d) show the formation of an ion pair in a catalyst (or initiator)AB, synthesized from two catalytic reagents A and B, as a rule introduced in the system. The catalytic or initiating pair then attacks the monomer and forms the first activated growing species. In the example c) boron fluoride forms an adduct with water in equilibrium with a polarized pair; this last can attack the monomer, giving rise to a cationic intermediate species. In the second example, from the reaction between sodium and liquid ammonia, an ion pair is obtained in equilibrium with sodium amide. This pair attacks the monomer and forms an anionic intermediate species.

These initiation stages are then followed by a number of additions of monomer and eventually to termination processes or processes equivalent to a termination.

The ionic or counterionic attack and the stereospecific polymerization A closer investigation of the chemical mechanism of an ionic polymerization makes clearer the mode of attack of the ion pair on the monomer.

An interesting classification of ionic polyadditions can be established on the basis of these investigations. As a matter of fact four limiting cases can occur, according to the following scheme:

Ionic Polyaddition

Conventional

cationic (ionic attack)

anionic (ionic attack)

Coordinated



cationic (counterionic attack)



anionic (counterionic attack)

We may note that, in the chemical attack to the monomer, the growing ion can be dominant: in this case the counterion is not important, and only assists the attack of the ion to the monomer. This type of polymerization may be called "conventional", or "by ionic attack". However, an opposite mechanism can take place, depending on the type of the ion pair and on the nature of the monomer and of the medium. The counterion can,

in fact, become relevant and determine the attack to the monomer. This attack in general occurs by the formation of coordinate bonds, and the corresponding polymerization may be called "coordinated", or "by counterionic attack". In these cases a coordination of the monomer to the counterion takes place first.

The most interesting and important feature of the coordinated polymerization is the possibility of obtaining, in the growing process, a complete control of many factors, which differently cause structural disorders in the polymer chain.

It is well known that polymer chains can be defective in many respects: branching, different arrangement of units along the chain, different configuration around particular atoms or groups, and so on. Almost all these defects can be, in principle, described in terms of isomerism phenomena, that is of isomeric changes of the units (or assembly of units) which take place at the same time as the addition of monomer molecules to the growing end of the chain.

The most important control, obtained in recent years, is the stereo control, that is the control of the possible steric isomerism of the polymer molecules around stereocentres located along the main chain, belonging to the base unit.

The stereocentres which have been so far important are ethylenic double bonds (as in 1, 4-polybutadiene) and carbon atoms, belonging to a saturated main chain, which are monosubstituted or differently disubstituted (as the tertiary carbon atoms of vinyl polymers).

Among the polymers containing the first type of stereocentre,
"cis-tactic" and "trans-tactic" polymers were obtained for which the same
cis or trans configuration is met along the chain with regard to all the
stereocentres. "Isotactic" and "syndiotactic" polymers were
synthesized among the polymers containing the second type of stereocentre,
in which the configurations around every stereocentre encountered along
the chain are either all identical or alternate.

All these polymers are also called in general "tactic polymers". Ditactic and tritactic polymers were also obtained in particular instances among the polymers which have in their base unit more than one stereocentre.

A polymer containing stereocentres, but devoid of a particular order in the steric configurations is called an "atactic polymer".

The great importance of the discovery of stereospecific macromolecular syntheses resides in the fact that different configurational isomers in the macromolecular compounds differ drastically in their physical, mechanical and thermal properties. Furthermore in many cases the suitable monomers are among the cheapest that the heavy chemical industry places at our disposal.

The most important difference between tactic and atactic polymers is, as a rule, the ability of the former to crystallise, and this accounts for the great difference in physical properties. However, in some instances, in which crystallinity is absent under practical conditions, the stereoregularity can be very important because of other determinant molecular properties. An example is that of rubber, which is used in the amorphous state, for which stereoregular diolefin polymers are in many respects superior to the non stereoregular ones.

The great importance of our ability to synthesize stereoregular polymers can be seen, from a scientific point of view, in our approach to the methods employed by Nature in many biological syntheses. The counterion coordinated polyaddition is, for example, very close to syntheses performed in Nature by enzymatic entities. In this way we have already been able to synthesize, by using asymmetric counterions, some polymers having optical activity. It is clear that in this field we have to expect the most important scientific developments of macromolecular chemistry in the relatively near future.

Copolymerization We have preferably dealt so far with the synthesis of homopolymers, but it is understandable that progress was also made in the synthesis of copolymers.

For these we are able to control, as a rule, the composition and all the factors that we can regulate in homopolymers. The greatest difficulty is today the fine or complete control of the disposition by which the different co-units follow each other along the copolymer chain.

The unit arrangements we are able to achieve today in synthetic copolymers can be represented, for the simpler case of binary copolymers having units A and B, as follows:

Types of unit arrangement

- A B A B A B A B A B A B A B A B alternating - A B B A B A A A B B A B A B A B B random - A A A A A A A A A B B B B B B B B segmented - A A A A A A A A A Agrafted B B B В \mathbf{B} B B B B B B B

The most regular arrangement is the first one, the so called "alternating copolymers", which, on the other hand, could seem to be in a sense a trivial one, in that such copolymers could be regarded as homopolymers having a single unit -A B-. The second one is a statistical arrangement, devoid of any order. The third one is that of the so called "segment" or "block" copolymers, in which the units are arranged in segments, each having units of the same type. The last one is the particular disposition of the so called "graft copolymers", in which "branches" of units of one type are grafted on a "trunk" consisting of units of the other type.

It is clear that different compositions and different unit arrangements lead to important differences in the properties of the corresponding copolymeric products, which exceptionally enlarge the application field covered by the homopolymers.

Replica polymerization Before concluding, it can be interesting to remember here one of the most important ways followed by Nature for synthesising copolymers, which can transfer complicated information through units arranged as a code.

The process has been called "replica" polymerization, in that the copolymer molecule is built by duplicating an already existing identical molecule. Replication takes place through the synthesis of an intermediate molecule which plays a role completely similar to that of a photo negative.

The principle of the synthesis of the intermediate molecule can be symbolically represented as follows:

1st Step	2nd Step	3rd Step	4th Step
1			i i
A D	ÁD	AD	A D
B B] BE		
I B E	 B E	 B E	F E
A D	ÅD	 Ap	Ĭ A D
A D	ÅD	 Ар	ļĨ
	1	, J.	A D
[[]	į	i i	

The pre-existing copolymer consisting of A and B units coordinates by weak side bonds (dotted in the scheme) molecules of two other monomers D and E, D having a selective affinity to units A, and E having a selective affinity to units B. The coordinated monomer molecules then find polymerization conditions, so that the intermediate molecule is formed and then released.

The similar subsequent synthesis by which, from the intermediate molecules consisting of units D and E, and monomeric species A and B, the initial macromolecule is duplicated, follows the scheme:

<u>1s</u>	t Step	2nd Step	3rd Step	4th	Step
¦ I D	А	р р А			
 E 	В	E B	DA 	D E	A B
É	В	EB I		É	 B
Ď	А	DA	D A	D D	 A
Ď ¦	A	D A	1	D 	A I

We are still unable to reproduce or simulate "replica" polymerizations in the laboratory. This type of synthesis would seem not very difficult to realize in the laboratory; on the contrary it is in fact very difficult to achieve the delicate, selective overall requirements of the coordination step. However it cannot be excluded that macromolecular syntheses of this type will be performed by Man in a not too distant future.



5. Electrochemistry

5. Électrochimie

Many recent school chemistry courses emphasize the importance of electricity as a form of energy which can bring about chemical changes. The electrolysis of a fused salt such as lead bromide gives pupils a vivid impression of these changes, and they can then go on to test the conductivity and the chemical changes in a wide variety of aqueous and non-aqueous systems. This can then lead to a study of metals as electrodes in simple cells and the construction of an "activity" series for these metals based on electrode potentials.

Electrochemical methods have been used on a large scale in industry for a long time, but there has recently been a great increase of interest in the development of electrochemical methods for the manufacture of a much wider range of chemical substances. It is important, therefore, that our students should have a clear idea of the role of electricity in chemical processes.

Two of the articles reproduced in this section are concerned, wholly or partially, with the process of electroplating. S. Yoneda points out some disadvantages in choosing nickel as an example for this process. Students in junior high school will not have heard very much about the chemistry of nickel and its compounds. Moreover, considerable care is needed to get satisfactory nickel plating. The electrolyte is a complicated mixture of substances whose function cannot be explained in simple terms to elementary classes. Dr. Yoneda shows how zinc can be plated in a satisfactory way from a slightly acidified solution of zinc sulphate, and he gives the necessary recipes and experimental details for this experiment. It has the great advantage that most pupils hear about zinc and its properties at an early stage in their course.

The article by J. Luneau is intended for students at a more senior level. He discusses various examples of anodic oxidation and cathodic reduction such as the preparation of persulphates, the industrially important anodic oxidation of aluminium, Nombreux sont les cours récents de chimie où l'on met l'accent sur l'importance de l'électricité en tant que forme d'énergie capable de provoquer des modifications chimiques. L'électrolyse d'un sel fondu comme le bromure de plomb rend ces changements parfaitement visibles aux élèves, et ils peuvent poursuivre l'expérience en vérifiant la conductibilité et les modifications chimiques dans un grand nombre de systèmes aqueux et non aqueux. Cela peut conduire ensuite à l'étude des métaux utilisés comme électrodes dans des piles électriques simples et à la construction d'une série « d'activité » pour ces métaux, fondée sur les potentiels d'électrodes.

Il y a longtemps que l'industrie utilise à grande échelle les méthodes électrochimiques, mais on a observé récemment une recrudescence d'intérêt pour la mise au point de méthodes électrochimiques en vue de la fabrication d'un beaucoup plus grand nombre de substances chimiques. En conséquence, il importe que nos élèves aient une idée claire du rôle de l'électricité dans les phénomènes chimiques.

Deux des articles reproduits dans la présente section sont consacrés, en totalité ou en partie, aux procédés de la galvanoplastie. S. Yoneda indique certains inconvénients qui s'attachent au choix du nickel comme exemple pour l'étude de ce procédé. Les élèves du premier cycle de l'enseignement secondaire ne savent pas grand-chose de la chimie du nickel et de ses composés. En outre, il est très difficile d'obtenir un dépôt de nickel satisfaisant. L'électrolyte est un mélange complexe de substances dont on ne peut expliquer la fonction en termes simples au niveau des classes élémentaires. Le Dr Yoneda indique comment on peut obtenir un dépôt de zinc satisfaisant à partir d'une solution légèrement acidifiée de sulfate de zinc, et il décrit l'expérience en détail, en donnant toutes les indications nécessaires sur la façon d'opérer. Le grand avantage de ce procédé est que la plupart des élèves ont entendu parler du zinc et de ses propriétés dès le début de leurs études de chimie.

L'article de J. Luneau est destiné à des élèves d'un niveau plus avancé. L'auteur étudie divers exemples d'oxydations anodiques et de réductions cathodiques, telles que la préparation des persulfates, l'oxydation anodique de l'aluminium. the passivation of iron, cathodic protection of metals from corrosion, nickel and silver plating.

A field of electrochemistry in which there is currently great development is in the design of fuel cells. A discussion of the principles governing the action of these cells involves a great deal of important physical chemistry. O. Lindström and I. Lindholm provide a clear account of the relevant theory at a level suitable for senior students and they describe the construction and operation of a simple fuel cell.

The paper by H. A. Neidig and his collaborators describes a series of experiments on the conductivities of electrolytes and the factors which can alter the conductivity. The article concludes with a set of eighteen penetrating questions on the results of the experimental work. A student who has worked through these should have a very clear idea of the relevance of specific and equivalent conductivities and the factors controlling their numerical values.

importante du point de vue industriel, la passivation du fer, la protection cathodique des métaux contre la corrosion, le nickelage et l'argenture.

Un domaine de l'électrochimie où l'on enregistre actuellement de grands progrès est celui de la conception des piles à combustibles. L'étude des principes régissant le fonctionnement de ces piles recouvre un domaine important de la chimie physique. O. Lindström et I. Lindholm donnent de la théorie applicable un exposé clair d'un niveau convenant aux élèves les plus avancés, et décrivent la construction et le fonctionnement d'une pile à combustible simple.

Dans leur article H. A. Neidig et ses collaborateurs décrivent une série d'expériences sur la conductivité des électrolytes et les facteurs qui peuvent la modifier. L'article se termine par une liste de 18 questions sur les résultats de ce travail expérimental. Un élève ayant travaillé ces questions devrait avoir une idée très claire de la signification des conductivités spécifiques équivalentes ainsi que des facteurs qui régissent leur valeur numérique.

ZINC PLATING AS A JUNIOR HIGH SCHOOL EXPERIMENT

by Shojiro Yoneda

A. Introduction

Both junior high school second year chemistry and senior high school chemistry deal with electrolysis. In junior high school chemistry metal plating experiments are done by students themselves, and the principle is explained in terms of the discharge of ions on the cathode.

We encounter many electroplated materials in our daily lives, and, therefore, we can expect great interest from our students in this topic when it is introduced into teaching.

The "Summary of Study Guidance" issued by the Ministry of Education lists "copper and nickel etc." as the examples of metal plating experiments, and therefore most textbooks describe nickel plating.

We have examined the problem whether or not nickel plating is suitable and effective as teaching material from the viewpoints of the chemistry involved and the difficulty of the experiment. We conclude that zinc plating is superior from all standpoints. Moreover, we have examined the zinc plating experiments as teaching material in detail, and have attempted some improvements. The results of this study will be described in this paper.

B. Metal Plating as Teaching Material

1. Nickel plating

Nickel is a white and beautiful metal extensively used for plating on the surface of various metals in order to give them good appearance and corrosion resistance. It is, therefore, likely that students have often seen nickel-plated products.

However, since students have not studied the chemical properties of nickel, there is no suitable means available for identifying the metal deposited when the theory of electro-plating is to be taught in terms of the transfer of ions (for instance, identification with dimethylglyoxime is possible, but not suitable here).

Furthermore, nickel plating requires great care over various technical points. For instance, the surface of the nickel anode becomes inactivated during the reaction and thus electrolysis become s impossible; nickel absorbs 11 to 13 times its own volume of hydrogen at ordinary temperature and 43 times at 70-80°C and the plated nickel tends to flake off because of this absorption of hydrogen. The plating is greatly affected by slight changes of the electrolyte; and the pretreatment of the metal is troublesome. Hence, it is not easy for a student to do a good nickel plating experiment.

The nickel plating solution described in most of the textbooks is that shown in Table 1. Ammonium chloride is added in order to increase the conductivity of the solution, and boric acid is added in order to adjust the pH of the solution. These substances are useful for improving the plating, but explanation of the reason for their addition is difficult for junior high school students. They may be confused by such explanations and may misunderstand the main point of the plating experiment. Since the object of the plating experiment is not to teach the technical details of the plating, due care should be taken in order not to confuse students.

Table 1

$NiSO_4^{7H_2O}$	15 g.
NH ₄ Cl	1.5 g.
H_3BO_3	1.5 g.
water	100 ml.
pН	5.6 - 6.0
$0.5 - 1.0 \text{ A/dm}^2$;	temperature higher than 18°C.

2. Zinc plating

Zinc plating is widely used as an excellent method of giving iron corrosion resistance. The acid zinc-plated steel has proved to be superior to the molten zinc-plated steel, and the zinc electro-plating is now used extensively. Because of the resistance toward sea water, acid zinc-plated steel is used for ships as well.

Students have learnt about zinc as a simple substance or as salts. They study "Hydrogen" in the first year, "Action of Acid on Metals", "Salts" and "Electric Cells" in the second year, and zinc ores in geology in the third year.

Though zinc is very familiar to students as explained above, it cannot be used as teaching material if zinc-plating is accompanied by some technical difficulties. But zinc-plating is easily carried out with very little expense. In order to develop this experiment further and to solve a few problems, a brief study has been made.

C. Acid Zinc Plating for Junior High School

1. Electrolyte

Various electrolytes have been reported for acid metal plating. As an example, Table 2 gives the electrolyte of a German method.

Table 2

$ZnSO_4.7H_2O$	250 - 400 g.
$MgSO_4$.7 H_2O	20 g.
$\text{Al}_2(\text{SO}_4)_3$ - XH_2 O	30 g.
H_3BO_3	20 g.
water	1 1.
pH	4.5
$2 - 6 \text{ A/dm}^2$; ordinary tem	perature

A small-scale plating was attempted in a beaker by use of this electrolyte, and a good result was obtained. However, it is difficult to explain to the students the reason for the addition of salts other than zinc sulphate, and it is likely that the students' questions may be focussed on this point. In order to remove these instructional difficulties, attempts have been made to do the plating in the presence of zinc sulphate only.

Figure 1 shows the electrolysis currents in 0.05 - 1.5M $\rm ZnSO_4$ solution in the absence of stirring. It has been found that a 0.5M solution possesses fair conductivity and is a suitable concentration.

Then the effects of the addition of various salts upon the electrolysis current are shown in Fig. 2. The figure shows that the addition of salts does not greatly affect the conductivity of the electrolyte.

2. Effect of the pH of the electrolyte

The major difference between the metal plated by a 0.5M zinc sulphate solution and the metal plated by the ordinary plating solution, is the appearance of the plated surface. The former is dark gray and dull, whereas the latter is grayish blue white and lustrous.

It has been found that the appearance of plated surface is greatly influenced by the pH of electrolyte. When commercial ZnSO₄·7H₂O is dissolved, the pH of the solution is about 4.5. When one drop of 1:1

sulphuric acid is added to 200 ml. of 0.5M $\rm ZnSO_4$ solution, the pH is lowered to 3. Plating with this solution has proved to yield a result as good as that obtained with the ordinary electrolyte.

Fig. 3 shows the change of pH as the electrolysis proceeds. It is clear that the pH of the $ZnSO_4$ solution with a drop of H_2SO_4 increases considerably during prolonged electrolysis, whereas the pH of the ordinary electrolyte is not much affected. Although the solution used in industry must maintain constant plating conditions for many hours, the solution is not used for more than 30 or 40 minutes in school experiments. Therefore, if the solution with one drop of sulphuric acid gives a result as good as the ordinary plating solution, this solution can be said to be quite valuable as a teaching material.

3. The electrolyte and the electrode

Fig. 4 shows electrolyses with a platinum anode and various cathodes. With a platinum cathode, the electrolysis voltage is 2.7 volts, but with a zinc cathode a very small voltage is sufficient for electrolysis.

A 100 ml. beaker was used as a small electrolysis cell. Both sides of the electrode are equally well plated when a copper cathode is placed more than 10 mm. away from the wall of the beaker and when the electrolysis is carried out in 100 ml. of 0.5M zinc sulphate (pH 3.5) using a small dry cell. Thus it has been shown that a small 100 ml. beaker can be used if a copper electrode of 6 cm² surface area is more than 10 mm. away from the wall of the beaker.

4. The temperature of the electrolyte

Fig. 5 shows the change of current with the temperature of the solution. The current changes greatly with temperature, but the appearance of the plated object is not much affected. This zinc plating can be carried out at room temperature in both summer and winter with good results, and there is no need to check the temperature, which is necessary in the case of nickel plating.

5. The purity of zinc sulphate

It is said that the purer the zinc sulphate the better the result of plating.

However, when zinc sulphate of reagent grade and extra pure grade are used with a cathodic current density of $3~\text{A/dm}^2$, there is no significant difference. But when zinc sulphate of industrial grade is used, the appearance of the product is gray and dull, and the polarographic study indicates the presence of cadmium. Thus it is better to use a reagent grade for the experiment.

6. Zinc plate as anode

A zinc plate can be obtained very inexpensively, whereas a nickel plate is very expensive. A zinc plate may be obtained from a used dry cell. In order to see whether or not a galvanized iron can be used, the thickness of the zinc layer was measured. The thickness of "Three Stars G 28 hot" was 12 - 13 μ , which is enough for use as an anode in this experiment.

D. Details of the Experiment

The solution is the one shown in Table 3. A drop of 1:1 sulphuric acid is added to 100 ml. of 0.5M zinc sulphate in a 100 ml. beaker. A thin copper plate (#32 - 34) of 1 x 3 cm. is hung using a light copper wire. The copper cathode is freed from surface deposit and oil with a brush and cleanser, washed with water, and then placed in the electrolyte. A galvanized iron the wall of the beaker. The electrolysis is carried out for 10 minutes using a dry cell.

Table 3.

$ZnSO_4 \cdot 7H_2O$	
4 Table 1 Tabl	15 g.
H ₂ SO ₄ (1:1) water	1 drop
pH	100 ml.
1 A/dm ² : room temperature	2.5 - 3.5
9.1175 action	

The copper plate changes colour to silver grayish blue during the electrolysis. When the direction of the current is reversed, one can observe that zinc falls off. When the zinc-plated copper is taken out from the cell, and is placed in dilute sulphuric acid, zinc dissolves to generate

hydrogen, and the reaction automatically stops when copper is exposed.

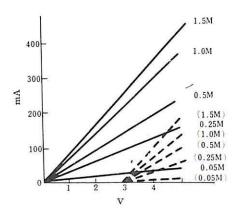
The amount of zinc deposited in 10 minutes is sufficient for the determination of the electrochemical equivalent using a triple-beam balance (sensitivity, 0.01 g.) (Fig. 6). As an alternative method, the amount of hydrogen evolved upon addition of acid to the zinc deposited can be measured volumetrically. This latter method does not require a balance, and only a burette is necessary.

If the voltage between two electrodes is kept low enough not to cause evolution of hydrogen at the cathode, the current efficiency approaches 100%. Therefore, this experiment appears to be applicable to senior high school chemistry as a quantitative experiment.

E. Summary

This experiment can be carried out with zinc sulphate as the only salt in a small 100 ml. beaker at room temperature within 10 minutes. Materials needed are small pieces of galvanized iron and copper plate and a dry cell. The appearance of the plated object is beautiful. It is pointed out that this zinc plating experiment is good teaching material in the junior high school chemistry since the principles of the metal plating can be explained very well by using this experiment.

It should be pointed out, however, that zinc plating on copper is not of industrial importance. Zinc plating on iron, however, is of great importance as a method of preventing corrosion.



Electrolysis at various concentrations. Fig.1. Zn , - - - Pt Anode:

Cathode: Pt Electrolyte: ZnSO₄ soln. Electrode surface 140mm²: Distance between

electrodes 60mm.

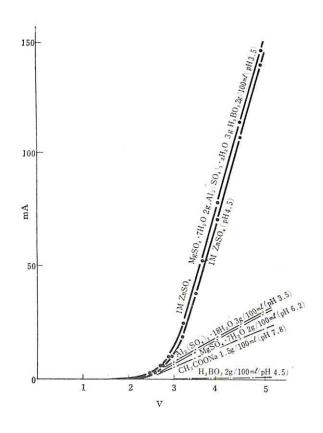


Fig.2. Electric conductivity with different additives

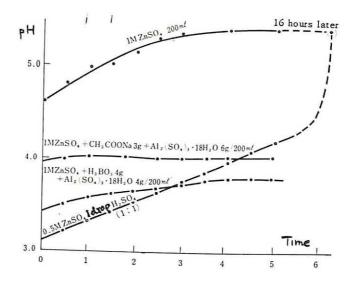


Fig.3. Change of pH with the progress of electrolysis. 200ml solution, 1.6V , 0.25A .

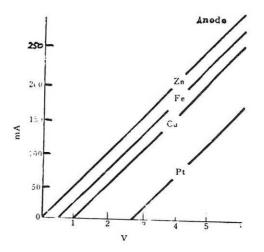


Fig.4. Electrolysis with various anodes. Cathode: Pt; 9.5M ZnSO₄soln.; pH 4.7; Temp. 16°C.; Surface 140mm²; 60mm between electrodes.

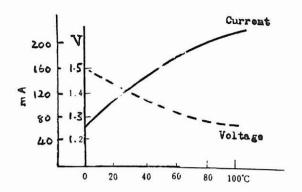


Fig.5. Temperature and current.
200ml beaker; 50mm between electrodes; 0.5M ZnSO₄
Cathode: 6mm² Cu; Anode: 6mm² Zn.

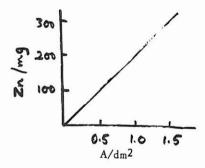


Fig.6. Zinc deposited after 10min electrolysis

A SIMPLE FUEL CELL FOR LECTURE EXPERIMENTS

by Olle Lindström and Ingemar Lindholm

Introduction The fuel cell belongs to the generation of galvanic cells that were developed during the first half of the nineteenth century with the Volta pile and the fundamental electrochemical investigations of Berzelius and Faraday as starting-point. Although the fuel cell has captured the imagination of the technologists for a century, its development has not made substantial progress until recently, and then mainly because the fuel cell has unique advantages as a power source for submarines, and on board space craft.

The difference between the fuel cells and the conventional galvanic cells - both of which can be called chemoelectric cells - are of a practical nature. The negative pole in a conventional cell, say the zinc cylinder in Leclanche's cell, is consumed on discharge. On the contrary, the negative pole in a fuel cell is not attacked and converts fuel supplied from outside. A fuel cell may thus be defined as a chemoelectric cell with an invariant electrolyte and invariant poles, oxidizing fuel supplied from outside with the liberation of electric energy for useful purposes.

Efficiency and Capacity The fuel cell is the only one of the unconventional sources of energy that is exempted from "the curse of the Carnot-cycle". The electric work performed by a galvanic cell

when consuming one mole of the reducing agent, the fuel, can be written nFE where n is the number of electrons transferred from a fuel molecule to the oxidizing agent, E is the electromotive force (emf; i.e. the cell voltage for reversible discharge) and F is 1 Faraday = 96500 coulomb. The product nF will thus be the electric charge moved between the poles at the oxidation of one mole of the fuel. In the electrolyte, this transport is effected by ions, in the outer circuit by electrons.

The electric work nFE equals the decrease of the free energy of the reaction - $\Delta G_{\mbox{\tiny J}}$ i.e.

- nFE =
$$\Delta$$
G = Δ H - T Δ S

Here ΔH is the enthalpy change, ΔS the entropy change and T the absolute temperature. The entropy term $T\Delta S$ is usually small compared to the enthalpy term ΔH . Theoretically, the electric work that can be gained will therefore often be nearly equal to the heat of combustion.

The ideal efficiency $\eta_{id}^{}$ for the fuel cell is given by the quotient between the theoretical yield of electric work, and the heat of combustion.

$$\eta_{\rm id}$$
 = nFE/(- Δ H) = 1 - T Δ S/ Δ H

In a hydrogen oxygen cell with an alkaline electrolyte, essentially the following reactions occur. The hydrogen is oxidised by hydroxide ions and emits electrons to the negative pole in the fuel cell.

$$H_2 + 2 OH^- \longrightarrow 2 H_2O + 2 e^-$$

The oxygen takes up these electrons at the positive pole of the fuel cell (the transport of electrons goes via the external circuit):

$$\frac{1}{2}$$
 O₂ + H₂O + 2 e⁻ 2 OH⁻

The net reaction is production of water,

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2 O$$

At 25°C, atmospheric pressure and condensation of the produced water -

 ΔG = -2.37 · 10⁵ J/mole, ΔH = -2.86 · 10⁵ J/mole and ΔS = -163 J/deg.mole. The emf will be E = 1.23 V and the ideal efficiency η_{id} = 0.83.

Existing fuel cells give emfs around 1 V; the sodium cell is the best one with nearly 2 V. In practical use the efficiency is lower than the ideal because of potential losses due to polarization and ohmic resistances. Of these the polarization losses, mostly due to inert electrode reactions, are often the more serious ones. The best hydrogen oxygen cells have, however, an efficiency of around 0.75 at reasonable current densities.

The Hydrogen Oxygen Cell Many types of fuel cells are being developed. The great number of different types is caused by the fact that there are many different fuels to choose from. Hydrogen gas is however a very superior fuel for fuel cells. The light hydrogen gas molecule is rapidly transported to the sites of reaction in the electrode and is easily oxidized without complicated side reactions. A number of catalysts, ranging from nickel boride to platinum, are effective in promoting this reaction. The product of the reaction, namely water, can easily be removed so that the reaction sites are not blocked. The hydrogen cell also has a specific power nearly ten times higher than that of cells for other fuels with the exception of some exotic cells, like the sodium battery. The hydrogen gas cells are today also the only ones that are ripe for marketing.

In fuel cells, porous electrodes are as a rule used. These have a large inner catalyst surface and can therefore give a high current density counted on the geometrical electrode used. For the manufacture of such electrodes very special arrangements are needed. In the simple hydrogen oxygen cell described here, on the other hand, the electrodes are easily prepared from rolled nickel gauze, treated with a platinum catalyst.

The electrode reaction occurs near the gas-liquid interface. Gas molecules dissolve in the thin film formed by the electrolyte on the electrode, diffuse through the liquid phase to the electrode surface, are adsorbed and react electrochemically.

The reaction rate per surface unit is actually just as fast for this fuel

cell as for one with porous electrodes but as the contact surface is small and the cell has a high ohmic resistance, the produced current is low.

Material Nickel gauze around 120 mesh. One g. platinum (IV) chloride. U- or H-tube (glass). Two wash-bottles. Two rubber stoppers for the U-tube, each with two borings for thin glass-tubes. Hydrogen and oxygen. Voltmeter. Ammeter. Variable resistance, ca 100 Ohm. Electric leads and connections.

Assembling the Cell It is necessary to wear protective glasses when making and testing the cell because of the risk of alkaline spills.

Two strips are cut from the nickel gauze, around 50 mm. wide and with a 10 mm. wide protruding part, long enough to reach out of the U-tube (Fig. 1). The strips are rolled into spirals that fit into the U-tubes.

One g. of platinum (IV) chloride is dissolved in ca 100 ml. 2 M HCl in a tall beaker and heated to ca 60° C. The two nickel strips are lowered into the warm solution for 5 - 10 mins. A coating of platinum black is formed on the nickel gauzes, according to the reaction

$$PtCl_6^{2-}$$
 + 2 Ni \longrightarrow Pt + 2 Ni²⁺ + 6 Cl

The electrodes are taken out, washed and kept in distilled water. If the activation with platinum is done at room temperature the gauzes have to stay in the solution for an hour.

The U-tube is filled nearly half-way up with 5 M KOH. The electrodes are placed so that half of the spiral is immersed. Wash-bottles, inlets and outlets for gas are connected as shown in Fig. 2. The voltmeter is connected to the hydrogen and oxygen electrode. When hydrogen and oxygen slowly bubble past the electrodes the air is displaced and the voltage of the cells mounts to ca 1 V. The cell's capacity for work is measured with a circuit consisting of an ammeter and a resistance in series, as shown in Fig. 3. This circuit is connected once the cell voltage has reached about 1 V. When the current is increased the voltage falls off because of the potential losses due to the polarization of the electrodes and the inner resistance of the cell. An example of a polarization curve is found in Fig. 4.

Interesting electrocatalytic experiments can be performed with this type of fuel cell, e.g. tests of electrodes with palladium as a hydrogen and oxygen catalyst and silver as an oxygen catalyst.

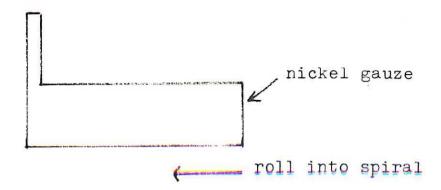


Fig.1. Shape of nickel gauze (120 mesh) before rolling into spiral

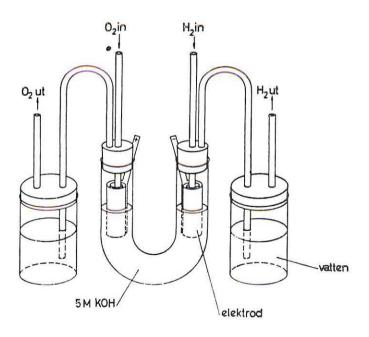


Fig.2. The assembled fuel cell

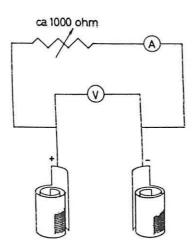


Fig. 3. Circuit diagram

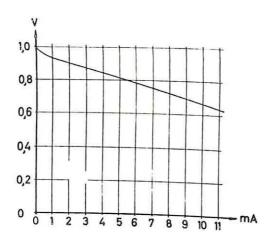


Fig.4. Polarisation curve



Quelques expériences simples d'oxydation anodique et de réduction cathodique

J. Luneau

Puisque l'oxydation et la réduction sont interprétées par des pertes ou des gains d'électrons, il est normal d'attacher une attention particulière aux processus de l'électrolyse où les pertes et les gains d'électrons se font le plus directement et le plus simplement, au contact de l'anode et de la cathode.

Certaines expériences d'électrolyse sont des plus courantes et leur interprétation peut se trouver dans tous les manuels : électrolyse des solutions de chlorure de sodium ou de soude, des solutions d'acide sulfurique ou de sulfate de cuivre. D'autres, qui sont réalisées plus rarement dans nos cours ou nos travaux pratiques, ne nécessitent cependant qu'un matériel des plus restreints et peuvent constituer d'excellents exemples d'oxydations anodiques et de réductions cathodiques, en même temps qu'elles illustrent de nombreuses autres notions : potentiels d'électrode ou d'oxydo-réduction, constante de stabilité d'un ion complexe, passivation par oxydation... etc.

Je me suis efforcé, en m'aidant de documents relatifs à certains procédés industriels, de mettre au point quelques expériences qui pourraient être regroupées en une manipulation unique ou séparées pour être rattachées à des manipulations relatives à l'étude des propriétés de certains corps : aluminium, fer, cuivre, acide sulfurique et sulfates...

Matériel utilisé pour les expériences :

Accumulateur de 6 volts ou 12 volts. Rhéostat de 30 ohms. — Apèremètre 0-2 ampères. Verres à précipités et tubes en U (diamètre 2 cm).

Lames métalliques de laiton et d'aluminium, de longueur 10 cm et de largeur 1 ou 2 cm.

Pointes de fer de longueur 10 cm.

Exemples de réductions cathodiques :

Les réductions cathodiques les plus simples sont celles qui correspondent à la décharge d'un ion métallique sur la cathode

$$M^{n+}$$
 + ne \rightarrow M^{o}

Le dépôt métallique est en principe très facile à obtenir à partir d'un sel du métal. Si l'on veut cependant obtenir un beau dépôt bien brillant et à l'aspect incontestablement métallique, de nombreuses précautions sont à prendre (nature et état de la lame sur laquelle se fait le dépôt, nature de l'électrolyte, densité de courant, température). Les dépôts de nickel et d'argent me paraissent être à la fois les plus simples à obtenir et les plus beaux.

Nickelage:

On obtient un très bon nickelage, brillant et adhérent sur plaques de laiton (électrodes 10 cm × 2 cm) préalablement décapées avec une solution de soude, en utilisant comme électrolyte le sulfate de nickel ammoniacal. A la solution de sulfate de nickel à 200 g/litre de sel cristallisé. on ajoute progressivement la solution ammoniacale jusqu'à redissolution complète du précipité d'hydroxyde formé et obtention d'un liquide bleu foncé. Les lames électrodes sont presque intégralement immergées dans la solution, un becher sert de cuve à électrolyse ; le générateur est un accumulateur de 6 volts. La distance des électrodes étant de 4 cm, on règle l'intensité de façon à réaliser une densité de courant de quelques ampères par dm2 de surface de plaque. Après quelques minutes, le dépôt est obtenu; on l'essuie et on le rend brillant en le frottant légèrement avec un chiffon enduit de produit à polir.

Si l'on utilise la solution ordinaire de sulfate de nickel ou si l'on force la densité de courant, on obtiendra un dépôt très rapide, mais il sera rugueux et parfois peu adhérent.

Argenture :

La réduction électrolytique des ions Ag⁺ et le dépôt du métal sur une cathode de laiton (ou de cuivre) présentent des particularités intéressantes. Les potentiels normaux d'électrode (pris par rapport à l'électrode normale à hydrogène) sont en effet les suivants, pour les 2 métaux entrant dans la composition du laiton et pour l'argent :

$$Zn/Zn^{++}$$
: E = -- 0,762 volt; Cu/Cu^{++} : E = + 0,344 volt
 Ag/Ag^{+} : E = + 0,798 volt

Le zinc et le cuivre ont donc tendance à réduire les ions argent, c'est-à-dire à déplacer le métal de ses sels, selon une réaction d'oxydoréduction du type :

$$Cu^{\,\circ} \ + \ 2 \ Ag^{\scriptscriptstyle +} \rightarrow Cu^{\scriptscriptstyle ++} \ + \ 2 \ Ag^{\,\circ}$$

Il semble donc qu'il n'y ait besoin d'aucune force électromotrice extérieure pour réaliser l'argenture. Effectivement, si l'on plonge une lame de laiton dans une solution de nitrate d'argent (à 20 grammes/litre) elle se recouvre immédiatement d'un dépôt d'argent, mais ce dépôt n'a nullement l'aspect métallique, il est brun, présente un aspect boueux et n'a aucune adhérence. La raison en est que la différence de potentiel entre l'électrode et la solution est trop grande, que les ions argent sont aussi en trop grand nombre, d'où un dépôt trop rapide qui ne permet pas aux cristaux du métal de se former et de se développer normalement.

Il va donc être possible de modifier ces conditions. Le potentiel d'électrode de l'argent dépend en effet de l'activité, donc de la concentration des ions Ag^+ , selon la formule :

$$E = Eo + \frac{RT}{F} Log \alpha$$

où Eo est le potentiel d'électrode pour une solution normale (activité des ions Ag^+ égale à 1) et α est l'activité des ions Ag^+ dans la solution considérée. Il suffit donc de diminuer α pour diminuer E, et pour éventuellement même en changer le signe. La façon la plus simple de diminuer considérablement α (c'est-à-dire en fait la concentration des ions) est d'engager les ions Ag^+ dans des ions complexes suffisamment stables.

Un premier essai peut être réalisé avec les ions argentiammines. On ajoute donc la solution ammoniacale au nitrate d'argent, jusqu'à ce que le précipité d'hydroxyde d'argent apparu soit entièrement redissous. Plongeant une lame de laiton dans la solution du sel complexe, on constate qu'il se produit encore spontanément un dépôt d'argent. La lame reste donc réductrice par rapport aux ions argent. Le potentiel d'électrode Ag/Ag⁺ n'a pas été suffisamment abaissé, car la constante de stabilité de l'ion complexe [H₃N - Ag⁺ - NH₃] formé est seulement de l'ordre de 10⁻⁸ :

$$(Ag^{+})$$
 $(NH_3)^2 = 6.3.10^{-8} ([H_5N - Ag^{+} - NH_3])$

Les ions Ag⁺ libres sont donc encore nombreux et leur activité n'est pas encore assez faible. On observe cependant que le dépôt obtenu se produit plus lentement et qu'il commence à présenter un aspect nettement métallique, mais il manque d'adhérence et disparaît par frottement avec un papier filtre.

Adressons-nous alors à un autre complexe plus stable. En versant du cyanure de potassium dans la solution de nitrate d'argent, nous obtenons d'abord un précipité de cyanure d'argent qui se redissout dans un excès de cyanure alcalin. Plongeons à nouveau la lame de laiton dans la solution; le dépôt d'argent ne se produit plus; les métaux constituants du laiton — cuivre et zinc — ne peuvent donc plus réduire les ions Ag+. Les ions complexes [Ag+(CN-)2] qui se sont constitués ont cette fois une constante de stabilité qui est de l'ordre de 10-21; le nombre d'ions Ag+ libres est extraordinairement faible et le potentiel d'électrode pour l'argent a changé de signe. Dès que quelques ions argent se sont déchargés et ont été remplacés dans la solution par des ions zinc Zn+2, la réduction des ions Ag+ s'arrête car le potentiel d'électrode de l'argent étant devenu supérieur à celui du zinc (en valeur absolue) c'est la réaction inverse:

$$2 \text{ Ag} + \text{Zn}^{+2} \rightarrow 2 \text{ Ag}^{+} + \text{Zn}$$

qui tend à se produire.

Il faudra donc dans ce cas l'intervention d'une force électromotrice extérieure pour produire le dépôt d'argent ; c'est dans ces conditions nouvelles que pourra être réalisée la « réduction cathodique » de l'argent.

Les conditions expérimentales seront analogues à celles utilisées pour le nickelage; l'électrolyte étant constitué par la solution du cyanure complexe d'argent et de potassium; la densité de courant ne dépassera pas non plus quelques ampères par dm². On obtient au bout de quelques minutes un beau dépôt d'argent lisse et adhérent qu'un coup de produit à polir rendra très brillant.

Remarques: a) Dans le cas du nickelage, les conditions du dépôt avaient également été modifiées (concentration des ions Ni⁺⁺ au voisinage de l'électrode, potentiel de l'électrode) en engageant les ions nickel dans les ions complexes nickelhexammine [Ni⁺⁺(NH₃) 6] et la qualité du dépôt s'en était trouvée améliorée.

b) Pour l'interprétation des phénomènes, il serait sans doute plus simple d'utiliser une cathode de cuivre pur plutôt qu'une lame de laiton, alliage de 2 métaux. Les dépôts obtenus sur le cuivre rouge présentent aussi un bon contraste et sont bien adhérents.

Autres réductions' cathodiques :

La réduction cathodique ne se limite pas toujours au cas très simple de la décharge totale d'un ion métallique avec dépôt du métal. On peut aisément réaliser des réductions un peu plus complexes.

Réduction d'un sel ferrique à l'état de sel ferreux :

On réalise l'électrolyse d'une solution de chlorure ferrique + acide chlorhydrique dans un tube en U avec une faible densité de courant (électrodes inattaquables de platine ou de graphite). En opérant périodiquement avec une pipette des prélèvements de liquide au voisinage de la cathode, on observe la transformation graduelle du sel ferrique en sel ferreux :

$$Fe^{+3} + e^{-} \rightarrow Fe^{+2}$$

Réduction électrolytique de l'acide nitrique :

La solution électrolytique est un mélange à parties égales d'acide nitrique concentré et d'acide sulfurique concentré; on opère dans un tube en U avec une anode inattaquable et une cathode constituée par une lame de plomb décapée. En opérant avec une forte densité de courant (20 Ampères par dm²) l'acide nitrique au voisinage de la cathode sera réduit jusqu'au stade ammoniac, que l'on pourra caractériser par ses réactifs habituels sur des prélèvements effectués près de cette électrode :

$$NO_{3}^{-} + 9H^{+} + 8e^{-} \rightarrow NH_{3} + 3H_{2}O$$

La protection cathodique de certains métaux dont nous parlons pour finir, se rattache également à ces processus de réduction cathodique.

Exemples d'oxydations anodiques :

Symétriquement au cas des cations, les oxydations anodiques les plus simples correspondront au retour d'un anion simple (Cl-, Br-, I-) au corps dont il est issu. Ces exemples sont bien connus, il est bon de remarquer néanmoins que l'oxydation des ions I- à l'état d'iode libre brun, qui se produit abondamment dans l'électrolyse de l'iodure de potassium (utiliser un tube en U avec une anode de graphite) est sans doute plus spectaculaire que le dégagement du chlore dans l'électrolyse du chlorure de sodium.

On peut cependant très facilement réaliser des oxydations anodiques plus complexes. Passage des ions sulfate aux ions persulfate :

On prépare une solution à 200 grammes/litre de sulfate de potassium à laquelle on ajoute un peu d'acide sulfurique. L'électrolyse a lieu dans un tube en U avec des électrodes inattaquables (petites lames de platine); la densité de courant est aussi élevée que possible (quelques dizaines d'ampères par dm²). On vérifie préalablement que la solution n'a pas d'action sensible sur l'iodure de potassium. Après un quart d'heure de passage du courant (il est indiqué de refroidir le tube à électrolyse avec de la glace), on opère à l'aide d'une pipette un prélèvement du liquide voisin de l'anode. Versé dans une solution d'iodure de potassium additionnée d'empois d'amidon, ce liquide fait virer instantanément au bleu l'empois d'amidon qui décèle ainsi la présence d'iode libre; la coloration ne cesse de s'intensifier au cours du temps.

Cette réaction d'oxydation des ions I- de l'iodure de potassium (obtenue cette fois en dehors de l'appareil à électrolyse) caractérise la présence dans le compartiment anodique d'ions oxydants, qui sont les ions persulfate, provenant eux-mêmes de l'oxydation des ions sulfate :

$$_{2}SO_{4}^{--} \rightarrow S_{2}O_{8}^{--} + 2e$$

Les autres réactions des ions persulfates peuvent être aussi vérifiées (oxydation de l'hydroxyde manganeux Mn (OH)₂ blanc en MnO₃H₂ noir, formation, lorsqu'on ajoute un peu de soude à une solution contenant à la fois du nitrate d'argent et la solution obtenue à l'anode, d'un anneau noir de peroxyde d'argent Ag₂O₂.

Cette méthode est utilisée pour la préparation électrolytique des persulfates qui sont eux-mêmes des intermédiaires pour l'obtention de l'eau oxygénée. Il n'a cependant pas été possible de déceler dans nos expériences la formation d'eau oxygénée en quantité appréciable à l'anode : les réactions spécifiques de H₂O₂ (avec le sulfate de titane par exemple) sont restées négatives.

Oxydation anodique (anodisation) de l'aluminium :

Elle est pratiquée couramment dans l'industrie pour assurer la protection du métal contre la corrosion, et éventuellement son isolement électrique, grâce au renforcement de la pellicule d'alumine. Les électrodes utilisées seront des lames d'aluminium à 99,5 %, bien débarrassées sur les bords des bavures provenant de la coupe, légèrement décapées à la soude et bien rincées à l'eau. Le liquide

électrolytique utilisé est une solution d'anhydride chromique CrO_3 à 6 %, à laquelle on a ajouté un peu d'acide sulfurique (on peut aussi employer simplement une solution sulfurique à 20 %). On établit entre les électrodes distantes de quelques centimètres une d.d.p. croissant progressivement de 4 à 20 volts. L'intensité du courant baisse rapidement, par suite de la polarisation, puis se stabilise à 0,1 ou 0,2 ampères. On peut arrêter l'opération au bout de 10 minutes, car l'épaisseur de la couche d'alumine a déjà atteint une dizaine de microns.

Il est possible de montrer le rôle protecteur de cette pellicule d'alumine — qui a poussé de l'intérieur vers l'extérieur sous l'action de l'oxygène produit par électrolyse dans tous les pores de la couche — par l'expérience suivante : une lame ayant servi d'anode et une lame ayant servi de cathode sont introduites dans 2 tubes à essais contenant une solution diluée d'acide chlorhydrique (même concentration pour les 2 tubes). La lame cathode est presque instantanément attaquée, avec dégagement de bulles d'hydrogène; l'attaque du métal de la lame anode, caractérisée par la formation des bulles d'hydrogène, ne démarre qu'après un temps assez long (parfois plusieurs minutes). Il a fallu préalablement dissoudre la pellicule d'alumine renforcée qui recouvre le métal et cette dissolution est assez lente.

Le rôle d'isolant très efficace joué par la pellicule d'alumine renforcée peut aussi être très facilement mis en évidence. Un circuit électrique comprenant un accumulateur, un rhéostat, un ampèremètre est fermé par un contact entre 2 lames d'aluminium tenues par des pinces crocodile qui terminent les conducteurs extrêmes de la chaîne. Si l'on établit le contact entre 2 lames d'aluminium non traitées ou 2 lames ayant servi de cathodes, le courant passe; si l'on utilise 2 lames « anodisées » aucun courant ne passe, même si les 2 lames sont serrées fortement l'une contre l'autre (à condition qu'elles ne présentent pas de bavures).

Un résultat meilleur encore sera obtenu si l'on « colmate » la couche d'alumine des lames anodisées en les laissant séjourner un quart d'heure dans de l'eau déminéralisée à l'ébullition; le léger gonflement de l'alumine qui en résulte entraîne l'obturation de tous les pores de la couche, la rendant ainsi imperméable et accroissant son pouvoir d'isolement et de protection.

Ajoutons que la couche d'alumine développée par oxydation anodique peut fixer de nombreux colorants qui modifient l'aspect du métal et permettent des effets décoratifs variés.

Passivation du fer par oxydation anodique :

La même solution (acide chromique + un peu d'acide sulfurique) peut être utilisée pour obtenir la passivation du fer par oxydation anodique. On peut prendre pour électrodes de longues pointes de fer polies à la toile émeri fine et lavées avec une solution de soude. Après un quart d'heure de passage du courant (densité : quelques ampères par dm²) la pointe anode est devenue passive à l'acide nitrique dilué comme si elle avait séjourné dans l'acide nitrique fumant. La passivité se prolonge pendant un temps très variable d'une expérience à l'autre ; elle cesse instantanément si l'on touche avec un fil de cuivre la partie anodisée de la pointe que l'on a immergée dans l'acide.

L'explication de cette passivation est la même que celle que l'on donne pour la passivation conférée par l'acide nitrique fumant : une légère pellicule protectrice (Fe₂O₃ ou Fe₃O₄ s'est formée par oxydation anodique du métal ; cette couche est compacte, continue et pratiquement insoluble dans les acides. On peut d'ailleurs signaler que des pointes bleuies à la flamme — c'est-à-dire recouvertes d'une mince couche d'oxyde magnétique Fe₃O₄ — sont également passives vis-à-vis de l'acide nitrique dilué (si le bleuissement a été réalisé sur toute leur surface).

Protection cathodique des métaux :

Si l'on plonge dans de l'eau de Javel étendue des pointes de fer, des points de rouille apparaissent après quelques minutes et la rouille continue à gagner rapidement autour de ces premiers centres. L'eau de Javel, en raison de ses propriétés oxydantes, est pour le fer un liquide particulièrement agressif.

Reprenant une pointe intacte et bien décapée, on la relie par un fil d'aluminium à une lame d'aluminium et on place l'ensemble dans la même eau de Javel étendue, la pointe de fer étant complètement immergée. La pointe ne rouille plus, même après plusieurs jours de séjour dans la solution. Une pile s'est constituée avec les 2 électrodes et l'eau de Javel, et celle-ci est lentement électrolysée. Des deux métaux, le plus électropositif est l'aluminium; c'est donc lui qui passe à l'état d'ions; par le fil extérieur, les électrons iront de l'aluminium vers le fer et c'est sur ce métal que se déchargeront les cations H*. Le milieu devien-

dra donc réducteur du côté du fer, oxydant du côté de l'aluminium, ce qui explique la protection assurée au fer contre la corrosion.

Des dispositifs basés sur cette propriété sont utilisés pour protéger contre la corrosion de l'eau de mer les hélices marines et même les coques de bateaux par l'emploi comme électrodes de protection de plaques d'aluminium, ou mieux de magnésium. Il s'agit encore dans ce cas d'une application des réactions d'oxydation anodique et de réduction cathodique.

Remarque — Dépôt anodique d'un métal :

Réalisant des argentures électrolytiques sur cuivre avec un bain de cyanure d'argent dissous dans la solution de cyanure de potassium, j'ai eu la surprise au cours d'une expérience, de voir le dépôt d'argent apparaître sur la lame anode. Pour aussi étonnant qu'il paraisse, le phénomène est bien connu et l'interprétation en est simple. Lorsque la différence de potentiel est établie (V petit), les anions complexes [Ag+ (CN-)2] se déplacent de la cathode vers l'anode; du côté de la cathode, la concentration des ions argent libres est beaucoup trop faible et la d.d.p. cathode/solution trop petite pour que la réduction des ions argent et le dépôt du métal puissent se produire. Du côté de l'anode vont arriver par contre des ions complexes qui, déchargés, vont libérer des ions Ag+ dont la concentration va de ce fait sensiblement augmenter, étant donnée la différence des potentiels normaux d'électrodes de l'argent et du cuivre, le potentiel auquel est porté l'anode de cuivre n'est pas suffisant pour s'opposer à la réaction de réduction des ions argent, devenus trop nombreux, par Cu: $2 \text{ Ag}^+ + \text{Cu} \rightarrow \text{Cu}^{++} + 2 \text{ Ag}.$

Dans ces conditions, c'est donc l'anode qui se recouvre du dépôt argent.

Si l'on augmente la d.d.p. entre les 2 électrodes, le dépôt d'argent se fera normalement sur la lame de cuivre cathode. Pour une d.d.p. intermédiaire, ce dépôt s'observe simultanément sur les 2 électrodes.

Je me suis efforcé de retrouver les conditions à réaliser pour obtenir le dépôt purement anodique de métal que j'avais observé fortuitement au cours d'une expérience ; les limites dans lesquelles on peut observer le phénomène se sont alors révélées assez serrées.

Des résultats satisfaisants ont été obtenus dans les conditions suivantes :

Solution étendue de nitrate d'argent (de l'ordre de 1 gramme par litre).

Grand excès de solution de cyanure de potassium ajouté après redissolution du précipité de cyanure d'argent.

Récipient pour l'électrolyse : tube en U de diamètre 2 cm et de hauteur 15 cm (avec un tel tube les régions anodique et cathodique sont suffisamment séparées).

Différence de potentiel anode - cathode (réglée à l'aide d'un potentiomètre) : entre 0,1 et 0,2 volt.

Intensité du courant d'électrolyse : de l'ordre de 1 milliampère.

Les électrodes sont des lames de cuivre d'épaisseur 1 mm, de largeur 16 mm, de longueur 80 mm.

Un dépôt argenté brillant et très adhérent est alors obtenu uniquement sur l'anode, faisant contraste avec la couleur du cuivre gardée sur la partie de la lame non immergée dans la solution, la cathode conserve sans aucune modification la coloration initiale du cuivre rouge.

Je serais reconnaissant aux lecteurs du B.U.P. de toutes les indications qu'ils pourraient me communiquer sur des conditions différentes de réalisation de cette expérience et d'une façon générale sur les circonstances qui se prêtent le mieux à l'observation de dépôts anodiques de métaux.



Electrical Conductance and Interaction of Ionic Solutions LAB BENCH

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A group of students interested in the problem of interaction in chemical systems considered studying the electrical conductance of solutions of ionic compounds. After a thorough literature search, they decided that the following theoretical and experimental considerations were pertinent to their proposed study.

When an ionic compound is dissolved in water, the substance dissociates, forming hydrated ions. If two platinum electrodes, connected to an ammeter and to a source of electric energy such as a dry cell, are immersed in the resulting ionic solution, the ammeter indicates that electric charge is flowing through the circuit. Because the ionic solution is a part of the electric circuit, the solution must therefore be capable of conducting an electric charge. As a first approximation, the degree to which an ionic solution conducts an electric charge is an indication of the number of charged species present in the solution. This can be measured by finding the electrical conductance or the electrical resistance of the solution. But how does one measure. conductance or resistance?

CALCULATING SPECIFIC CONDUCTANCE

If the quantity of electric charge (I) flowing through an ionic solution is proportional to the voltage (E) applied to the platinum electrodes, a resistance (R) can be calculated for the system using Equation 1:

$$I = (1/R)E \tag{1}$$

where 1/R is a proportionality constant. The resistance of the ionic where 1/R is a proportionality constant. The loss-tance of the ionic solution between the platinum electrodes depends upon the cross-sectional solution between the platinum electrodes (/) between them. solution between the platfiam the distance (1) between them. These area (A) of the electrodes and the distance (2) relationships are shown in Equation 2:

$$R = \rho(\ell/A) \tag{2}$$

the specific resistance (ρ) is the resistance of the ionic solution the specific resistance (p) is the specific solution between two parallel platinum electrodes, each having a cross-sectional between two parallel platinum electrodes of low Theorem and the specific resistance of low Theorem and the specific between two parallel platinum steeds, such making a cross-sectional area of 1 square cm. and separated by a distance of 1 cm. The specific area of 1 square cm. and separated by a defined as the reciprocal section of the square cm. area of 1 square cm. and separated 3, a defined as the reciprocal of conductance (K) of an ionic solution is defined as the reciprocal of the specific resistance (Equation 3):

$$K = 1/\rho \tag{3}$$

If Equations 1, 2, and 3 are combined, the relationships given by Equation 4 are obtained:

$$K = \ell/AR = (\ell/A)(I/E)$$
 (4)

Equation 4 indicates that specific conductance is equal to the electric Equation 4 indicates that specific solution between two parallel platinum charge conducted by an ionic solution area of each electrode charge conducted by an long spectional area of each electrode is 1 square electrodes when the cross-sectional area of each electrode is 1 square electrodes when the cross-sectional and the potential difference cm., the electrodes are 1 cm. apart, and the experimental cm., the electrodes are 1 cm. apart, and the experimental difference between the electrodes is 1 volt. Even if the experimental conditions between the electrodes is 1 volt. between the electrodes is I volc. Even I am oxperimental conditions differ from those given above, the calculated specific conductances for

$$\rho = ohm-cm.$$

$$K = Ohm^{-1}cm^{-1}$$

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¹ Present address, Longwood College, Farmville, Va.



various ionic solutions can be compared and interpreted in terms of the specified hypothetical conditions. Because the microscopic area of the electrodes may differ from the measured macroscopic cross-sectional area (length \times width) because of unevenness of the surface, the term ℓ/A in Equation 4 is generally treated as a cell constant. It is determined experimentally for each conductance cell by measuring the current and potential difference between the electrodes when the conductance cell contains an ionic solution of known specific conductance.

For the purpose of this investigation, the students decided that specific conductance was not the only way to consider the charge carrying capacity of ionic solutions. The specific conductance of solutions of an ionic compound of different concentrations varies because of the different quantities of the charged species present in the solution as a result of the dissociation of the ionic compound. The students believed that the data needed for this study should be such that the charge carrying ability of a given number of charged species at different concentrations could be compared.

EQUIVALENT CONDUCTANCE OF IONIC SOLUTIONS

If the complete dissociation of an ionic compound is assumed, a solution is said to contain one equivalent mass of an ionic solute if it dissociates completely in solution to produce Avogadro's number of unit positive charges and unit negative charges. The total number of ions in a solution containing one equivalent mass of completely dissociated solute is equal to Avogadro's number divided by the electronic charge on the cation plus Avogadro's number divided by the electronic charge on the anion. The number of unit charges in a solution is important in measuring the charge carrying ability of a solution of an ionic compound and not necessarily the number of ions, for various ions may carry different numbers of unit charges. For example, a solution containing an equivalent mass of potassium chloride will contain 6.02×10^{23} K+ ions and 6.02×10^{23} 10^{23} Cl⁻ ions giving a total of 12.04×10^{23} ions; a solution containing an equivalent mass of magnesium sulfate will contain $3.01 \times 10^{23} \ \text{Mg}^{+2}$ ions and $3.01 \times 10^{23} \text{ SO}_4^{-2}$ ions or a total of 6.02×10^{23} ions, but the total number of positive and negative charges is equal to that in the potassium chloride solution. One equivalent mass of any solute, if completely dissociated in solution, would provide the same effective charge carrying ability as one equivalent mass of any other completely dissociated solute in solution. Or one might say that the conductance of an ionic solution can be related to the number of equivalents of the charged species present in a given volume of solution. Thus, the students decided that the equivalent conductance of ionic solutions should be used in this investigation.

 $\Lambda = \frac{Cm^2}{ohm \ equiv.}$

Equivalent conductance (Λ) can be defined in terms of the specific conductance. The relationship is given by Equation 5:

 $\Lambda = K/c = (\ell/A)(I/cE)$ (5)

where c is the concentration of the ionic solution in equivalents per milliliter. The equivalent conductance is the quantity of electric charge in amperes that is conducted, under a potential difference of 1 volt by a volume of solution containing one equivalent of solute, between electrodes in a conductance cell where the electrodes are 1 cm. apart and of large enough cross section to accommodate the volume of solution. Even if the experimental conditions are different from those given above, the calculated equivalent conductance can be interpreted in terms of these specified hypothetical conditions.

The interaction between the various charged species in an ionic solution and between the charged species and the solvent can be considered on the basis of the observed equivalent conductance of an ionic solution. If there is sufficient interaction involving the charged species in solution, the equivalent conductance of the solution might be assumed to be less than if there were no interaction. However, there are two major factors contributing to the equivalent conductance—apparent

26 CHEMISTRY VOL 38 NO 10 degree of dissociation of the ionic compound and ionic mobilities of the charged species in solution.

The apparent degree of dissociation of the ionic compound is a measure of the fraction of the compound that is present in solution as charged species. Thus, the magnitude of the equivalent conductance could indicate the number of charged species present in an ionic solution. For compounds such as acetic acid the uncharged species present in the solution could be undissociated molecules. On the other hand, for compounds such as sodium chloride and magnesium bromide, the solutions might be expected to contain uncharged species (ion pairs) formed from the interaction of charged species. In either case, the equivalent conductance of such solutions would be less than if the compounds had completely dissociated into charged species.

Ionic mobilities (μ^+ and μ^-) are the velocities at which the ions move in a solution when they are subjected to an electric potential gradient of 1 volt per cm. Because the solvent exerts a viscous drag on the movement of the ions in a solution, mobilities of the ions are affected by their size. Smaller ions generally have larger mobilities than larger ions. If the charged species of an ionic compound interacts sufficiently with the solvent molecules, each ion will be surrounded by a shell of solvent molecules. If this interaction is strong enough so that the solvent shell moves with the ion, the effective size of the ion will increase. Thus, the mobility of the ion will decrease. Hence, the equivalent conductance of the solution will be less than if the ion were not surrounded by a solvent shell.

The mobilities of the ions are influenced not only by the interaction of the ions with the solvent but also by the interaction of the ions with each other. As a solution of a compound becomes more concentrated, the magnitude of the electrostatic forces between the ions increases. A given positive ion will on the average be surrounded by more negative ions than positive ions because of the attractive forces between ions of opposite charge. When a difference in electric potential exists between the platinum electrodes, the positive ion and the negative ions surtounding it will move in opposite directions. The attractive forces rounding it will move in opposite ions will retard the movement of the between the negative and positive ions will retard the movement of the ions toward their respective electrodes. Hence, the mobilities will decrease and the equivalent conductance of the solution will decrease. The magnitude of the decrease in the equivalent conductance should depend upon the magnitude of the electrostatic forces.

For a compound which dissociates to form one positive and one negative ion, the relationship between the equivalent conductance, the apparent degree of dissociation (α) , and the mobilities of the positive and negative ions $(\mu^+$ and $\mu^-)$ is shown in Equation 6:

$$\Lambda = F\alpha(\mu^+ + \mu^-) \tag{6}$$

F is the Faraday constant (96,500 coulombs eq. $^{-1}$). Experimentally, the separation of the effects of the apparent degree of dissociation of a substance from the effects of the mobilities of the ions is difficult. The magnitude of the equivalent conductance could be affected by either or both of these factors. Large variations of the equivalent conductance with concentration can often be ascribed to a change in the apparent degree of dissociation of the compound. These variations can be explained by a large difference in the number of charged species available to conduct the electric charge in the different solutions. The behavior of the equivalent conductance of solutions of compounds such as acetic acid or other slightly dissociated acids or bases is interpreted mainly in terms of differences in the apparent degree of dissociation of the various compounds. For solutions of compounds such as sodium chloride or magnesium bromide the interpretation of changes in the equivalent conductance with concentration in terms of the apparent degree of dissociation and the mobilities of the ions is more arbitrary.

Often the assumption is made that a compound is completely dissociated often the assumption is made that a compound is completely dissociated into charged species ($\alpha=1$). Changes in the equivalent conductance are then discussed in terms of changes in the mobilities of the ions. For some systems discussed in terms of changes in the equivalent conductance are discussed in terms of both

Na⁺
ion
Ction
Na⁺Clion pair

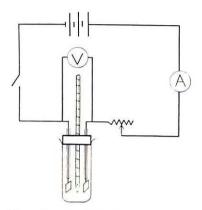


 $\mathcal{U}_{+} = \frac{cm^{2}}{\text{volt sec.}}$

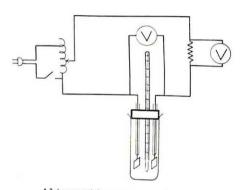
F= 96,500 coulombs equiv.

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CIRCUITS FOR DETERMINING THE CONDUCTANCE OF IONIC SOLUTIONS



Direct current circuit



Alternating current circuit

a change in the apparent degree of dissociation and a change in the mobilities of the ions. The effects of these changes can be separated by comparing the behavior of the equivalent conductance of the system being studied with the behavior of the equivalent conductance of a similar system in which the compound is considered to be completely dissociated.

Another factor that affects equivalent conductance is temperature. A change in the temperature of a solution of a compound could change the apparent degree of dissociation and the mobilities of the ions which could be reflected in the equivalent conductance.

After the students completed their literature search, they decided to divide their investigations into three parts. First, they wanted to find how the temperature would affect the equivalent conductance of lithium chloride, sodium chloride, and potassium chloride solutions. Then, they wanted to compare the effect of concentration on the specific conductance and on the equivalent conductance of solutions of potassium chloride and of acetic acid. Finally, they wanted to compare the interaction, as indicated by equivalent conductance, in the lithium chloride—water, sodium chloride—water, and potassium chloride—water systems.

EQUIVALENT CONDUCTANCE USING DIRECT CURRENT

Stock solutions were prepared of 1.00M potassium chloride solution, 1.00M acetic acid solution, 0.100M lithium chloride solution, 0.100M sodium chloride solution, and 0.100M potassium chloride solution with reagent grade chemicals and distilled water. Masses were determined using a Mettler balance, and volumetric flasks were used in preparing the solutions. Solutions of lower concentrations were prepared from the stock solutions by quantitative dilutions.

A circuit using direct current was constructed following the circuit diagram shown on the left. The circuit consisted of three 1.5-volt dry-cell batteries connected in series with a switch, an ammeter, a variable resistor, and the conductance cell (two platinum electrodes firmly positioned in a 180-ml. the conductance cell. The variable resistor was used to maintain a current of 0.50 ma. in the circuit.

In constructing the conductance cell it is important that the electrodes are rigidly mounted so that the distance and hence the conductance between the electrodes does not change after the cell constant has been determined. So that the effective area of the electrodes is not changed, it is important that the electrodes are immersed in the ionic solutions to be studied to the same extent as they were immersed when the cell constant was determined. One way of accomplishing this is to use the same volumes of solution for all determinations. A second method is to tubes, and then ensure that the platinum electrodes are completely covered for all determinations.

EFFECT OF TEMPERATURE ON EQUIVALENT CONDUCTANCE. A 150-ml. portion of 0.100M lithium chloride was placed

in the conductance cell into which a thermometer graduated in 0.1° C. units was also placed. The potential difference between the electrodes was measured at several different temperatures in the interval from 0° to 50° C. The procedure was repeated with 0.100M sodium chloride and with 0.100M potassium chloride solutions.

When a 0.100M lithium chloride solution was placed in the conductance cell, the potential difference between the platinum electrodes was 2.35 volts with the switch closed. When the switch was opened, the potential difference dropped almost immediately to about 2 volts, then decreased slowly to zero over a time period of about 3 minutes. Similar observations were made when the cell contained the other ionic solutions. One explanation of this behavior is that charge transfer at the platinum electrodes is accompanied by chemical reactions at the electrode surfaces

The chemical reactions occurring at the cathode (negatively charged platinum electrode) remove positively charged ions from the solution in the immediate neighborhood. The removal of positively charged ions results in a difference between the concentration of positively charged ions at the surface of the cathode and in the bulk of the solution and a difference between the net charge of the solution at the surface of the cathode and in the bulk of the solution.

The chemical reactions which occur at the anode (positively charged platinum electrode) remove negatively charged ions from the solution in the immediate neighborhood of the anode with similar results in the solution. The establishment of differences of ionic concentrations and net charge at each of the electrode surfaces is often referred to as polarization of the electrodes and could affect the measured difference in electrical potential between the two platinum electrodes. This action leads to the polarization of the electrodes.

Consequently, the validity of the conductances calculated from the measured potential differences using direct current is questionable. If the chemical reactions which occur at the electrode surfaces are reversible, the use of alternating current should reduce or eliminate the occurrence of differences in ionic concentration and net charge, because the effects of transferring charge for an instant from the electrode to the solution should be eliminated by the transfer of charge for an instant from the solution to the electrode. To eliminate the possibility of polarization, the investigation was continued using alternating current and platinum electrodes.

EQUIVALENT CONDUCTANCE USING ALTERNATING CURRENT

A circuit using alternating current was constructed following the circuit diagram shown on page 28. A variable transformer was used to maintain a potential difference of 3.00 volts across a 36.36-ohm standard resistor. Hence, the current in the circuit was held constant and was calculated to be 0.0825 ampere using Equation 1. A second voltmeter was used to measure the potential difference across

CONDUCTANCE DATA WITH ALTERNATING CURRENT CIRCUIT

Effect of Temperature

Ionic Soln., 0.100M	Soln. Temp., °C.	Potential Diff. between Electrodes, Volts
LiCl	4.06 16.52 24.59 34.22 45.61	6.42 4.91 4.37 3.70 3.21
NaCl	3.44 16.00 25.51 33.29 44.24	5.85 4.61 3.92 3.50 3.01
KCl	3.51 15.50 25.19 34.91 45.06	5.14 4.11 3.59 3.09 2.80

Effect of Concentration Using KCl

Ml. of 1.00 <i>M</i> KCl Added to 100.0 Ml. of Distilled Water	Potential Diff. between Electrodes, Volts
1.000	25.3
2.000	18.0
3.000	9.5
4.000	7.17
5.000	5.84
6.000	5.05
7.000	4.76
8.000	4.20
9.000	3.79
10.000	3.61

Effect of Concentration Using Acetic Acid

Soln. Conen., Moles/Liter	Potential Diff. between Electrodes, Volts
1.000	4.20
0.100	11.51
0.0100	33.7
0.00100	118.0

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the two platinum electrodes of the conductance cell when the cell contained a solution of an ionic compound.

The cell constant for the a.c. circuit was obtained by determining the potential difference between the platinum electrodes when the cell contained 0.100M potassium chloride at 25° C. The specific conductance of this solution is 0.01288 ohm $^{-1}$ cm. $^{-1}$ The potential difference between the platinum electrodes when the conductance cell contained this solution was 3.59 volts.

CAUTION. Extreme care must be taken when 110-volt alternating current is used. Careless use of this circuitry could result in serious injury or even death. At all times avoid touching the electrodes or exposed wire when an electric charge is passing through the circuit, especially when part of your body is near any metal object or other conductor connected to the earth such as water, steam, or gas pipes.

1. Calculation of cell constant $\frac{L}{A} = \frac{kE}{T} = \frac{0.01288 \text{ ohm cm.} \times 359 \text{ volts}}{0.0825 \text{ amp.}}$ $\frac{L}{A} = 0.560 \text{ cm.}^{-1}$

EFFECT OF TEMPERATURE. The data obtained using the a.c. circuit with platinum electrodes and the procedure described under the d.c. circuit for 0.100M solutions of lithium chloride, sodium chloride, and potassium chloride at different temperatures are given on page 29. EFFECT OF CONCENTRATION. A 100-ml. portion of distilled water was pipetted into the conductance cell A total of 100-100 water was

EFFECT OF CONCENTRATION. A 100-ml. portion of distilled water was pipetted into the conductance cell. A total of 10 1.000-ml. portions of 1.00M potassium chloride was added to the distilled water. The potential difference between the electrodes was determined after the addition of each portion of potassium chloride solution (page 29).

The potential difference across the 36.36—ohm standard resistor was maintained at 0.50 volt for the study of the acetic acid solutions. This corresponds to a current of 0.0138 ampere in the circuit. The potential difference between the platinum electrodes was measured when the conductance cell contained 1.00M, 0.100M, 0.0100M, and 0.00100M acetic acid and is given on page 29.

2. Calculation of

Aplcific Conductance
of 0.0100 M acetic acid $K = \frac{L \times I}{A \times E}$ 0.560 cm⁻¹ x 0.0138 amp.

33.7 volto $K = 2.29 \times 10^{-9}$ ohm⁻¹ cm⁻¹

QUESTIONS

The experimental data can be processed by answering questions 1-6 and can be interpreted by answering questions 7-14. To answer questions 15-18, additional information must be obtained either from the literature or by conducting a laboratory investigation.

- 1 Calculate the cell constant for the conductance cell used with the
- 2 Calculate the specific conductance of the potassium chloride solutions and of the acetic acid solutions from data given on page 29.
- 3 Calculate the equivalent conductance of each of the solutions studied with the a.c. circuit.
- 4 Plot the equivalent conductance obtained with the a.c. circuit of the 0.100M solutions of lithium chloride, sodium chloride, and temperature. Label this graph Figure 1.
- 5 Plot the specific conductance for the acetic acid-water system and the potassium chloride-water system on a graph of specific conductance vs. concentration. Label this graph Figure 2.
- 6 Plot the equivalent conductance obtained with the a.c. circuit for the acetic acid-water system and the potassium chloride-water system on a graph of equivalent conductance vs. concentration.
- 7 What effect does the temperature of the solution have on the equivalent conductance of 0.100M solutions of lithium chloride, sodium chloride, and potassium chloride? Interpret this behavior in terms of the effect of temperature on the apparent degree of

3. Calculation of

Equivalent Conductance
of 0.0/00 M acetic acid $C = \frac{1.00 \times 10^{-2} \text{equiv.}}{10^{3} \text{cm}^{3}}$ $1.00 \times 10^{-5} \text{Equiv. cm.}^{3}$ $1.00 \times 10^{-5} \text{equiv. cm.}^{3}$ $1.00 \times 10^{-5} \text{equiv. cm.}^{3}$ $\Lambda = \frac{K}{2} = \frac{2.29 \times 10^{-4} \text{ohm}^{-1} \text{cm.}^{-1}}{1.00 \times 10^{-5} \text{equiv. cm.}^{3}}$ $\Lambda = 22.9 \text{ cm.}^{2} \text{ ohm}^{-1} \text{equiv.}^{-1}$

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- dissociation of the ionic compounds and/or in terms of the effect of temperature on the mobilities of the ions.
- 8 Assume that the apparent degree of dissociation is approximately the same for lithium chloride, sodium chloride, and potassium chloride in a 0.100M solution. Account for the differences between the three curves in Figure 1 in terms of the differences of the mobilities of the ions. Rank the lithium, sodium, and potassium ions in order of their apparent ionic size based on the relative ionic mobilities. What explanation can be given to account for the order of apparent ionic size in comparison to the positions of the three elements in the periodic table?
- 9 What is the effect of concentration on the specific conductance of potassium chloride? Discuss in terms of the total number of potassium and chloride ions present in the system.
- 10 What is the effect of concentration on the equivalent conductance of potassium chloride? Discuss in terms of the effect of concentration on the apparent degree of dissociation of potassium chloride and/or in terms of the effect of concentration on the mobility of the potassium and chloride ions.
- 11 What is the effect of concentration on the specific conductance of acetic acid? Discuss in terms of the total number of ions present in the system.
- 12 What is the effect of concentration on the equivalent conductance of acetic acid? Discuss in terms of the effect of concentration on the apparent degree of dissociation of acetic acid and/or in terms of the effect of concentration on the mobility of the hydrogen and acetate ions.
- 13 Write a summarizing statement comparing the effect of concentration on the equivalent conductance of the two compounds, acetic acid and potassium chloride.
- 14 Write a summarizing statement comparing the effect of concentration on the specific conductance with the effect of concentration on the equivalent conductance.
- 15 Determine the equivalent conductance of solutions of sodium chloride, magnesium chloride, and aluminum chloride of various concentrations to determine the effect of ionic charge on the equivalent conductance.
- 16 Determine the effect of the size of the anion on the equivalent conductance by studying solutions of sodium chloride, sodium bromide, and sodium iodide. Discuss the results in terms of the relative ionic mobilities of the anions and their apparent ionic
- 17 Determine the effect of the solvent on the equivalent conductance of an ionic compound such as sodium iodide and on the equivalent or an ionic compound such as chloroacetic acid by using with conquerance of desired solvents such as water, methanol, ethanol, each solute different solvents such as water, methanol, ethanol, each Solute divane, or acetonitrile. Exercise the usual safety precautions when working with volatile solvents.
- 18 Devise an experimental procedure for using conductance to deter-Devise an experiment of the titration of a highly dissociated acid mine the end point of the titration of a highly dissociated acid mine the end positive of a solution of respective to determine with a highly dissociated base. Use this procedure to determine with a mighty determined to determine the reaction capacity of a solution of magnesium sulfate by the reaction supposed magnesium sulfate solution with a solution of barium titrating the magnesium sulfate solution with a solution of barium hydroxide of known concentration.

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6. Chemistry and industry

6. Chimie industrielle

Some teachers complain that too much emphasis is placed on industrial processes in school chemistry courses. They feel that many of these processes change so quickly that what is taught, and what appears in textbooks all too often bear no relation to current industrial practice. The fact that textbooks become out of date should not, however, deter us from attempting to relate our teaching to what goes on in the outside world.

The articles in this section have been chosen for their relevance to industrial chemistry. A. M. Neimark et al. emphasize the need that industrially developed and developing countries have for increasing numbers of trained technicians. They describe some interesting school courses in the U.S.S.R. which have a very definite slant to industrial chemistry. Perhaps the outstanding feature of these courses is the way in which work in school is supplemented by courses in the factory or research institute. Thus pupils can extend the techniques of analysis that they learn in the school laboratory by making use of a variety of instruments too expensive for a school laboratory but readily available in industry. The immense importance of chemistry in contributing to the alleviation of the world's food problems is an aspect of science that should appeal to idealistic young people. The article on the manufacture of the state of t facture of ammonia and the production of nitrogen fertilizers has been written by two chemists who work in industry. They describe the essential physical chemistry of the process and the recently developed method of preparing the necessary hydrogen from low-boiling fractions provided by petroleum refining which is particularly important for those countries lacking natural gas supplies.

The article by L. A. Kozyrev is concerned with industrial organic chemistry. He discusses the kind of material that should be introduced into school courses to relate them more closely to industrial developments. He suggests that this can be done by considering a limited number of typical reactions and typical pieces of industrial equipment, rather than by separa-

Certains enseignants se plaignent de ce que, dans les cours de chimie scolaires, une trop grande place soit faite aux procédés industriels. Ils pensent que beaucoup de ces procédés changent si rapidement que les notions enseignées et indiquées dans les manuels sont trop souvent sans rapport avec la pratique industrielle du moment. Mais le fait que les manuels se démodent ne doit pas nous empêcher d'essayer de rattacher notre enseignement à ce qui se passe dans le monde extérieur.

Les articles qui figurent dans la présente section ont été choisis pour leurs rapports avec la chimie industrielle. A. M. Neimark et al. soulignent que les pays industriellement développés comme les pays en voie de développement ont besoin d'un nombre de plus en plus grand de techniciens qualifiés. Ils décrivent certains cours intéressants donnés en URSS, qui sont très fortement orientés vers la chimie industrielle. La caractéristique la plus marquante de ces cours est peut-être la façon dont le travail scolaire est complété par des cours donnés dans les usines ou les instituts de recherche. De cette façon, les élèves peuvent développer les techniques d'analyse apprises en laboratoire à l'école en utilisant divers instruments trop coûteux pour un laboratoire scolaire mais qu'on trouve sans difficulté dans l'industrie.

Le rôle capital que peut jouer la chimie dans la solution du problème de la faim dans le monde est un aspect de la science qui devrait attirer les jeunes idéalistes. L'article consacré à la fabrication de l'ammoniac et à la production d'engrais azotés a été rédigé par deux chimistes qui travaillent dans l'industrie. Ils décrivent les principales réactions de chimie physique qu'implique ce procédé, ainsi que la méthode, récemment mise au point, qui permet de préparer l'hydrogène nécessaire à partir de fractions à point d'ébullition peu élevé produites par le raffinage du pétrole, ce qui est particulièrement important pour les pays dépourvus de réserves de gaz naturel.

L'article de L. A. Kozyrev traite de la chimie organique industrielle. L'auteur examine les questions qui devraient être introduites dans les cours scolaires pour les relier plus étroitement aux applications industrielles. Il estime qu'à cette fin, il est préférable d'étudier un nombre limité de réactions et de pièces d'équipement industriel types plutôt que

tely discussing the industrial preparation of a large number of substances. Thus he considers, with appropriate examples, hydrogenation and dehydrogenation, hydration, chlorination, alkylation, esterification, oxidation, isomerization and polymerization. Industrial chemistry need not be taught as a separate topic and these industrial examples can be woven into the school course where appropriate.

The article by T. C. Swinfen differs from the other articles in this volume in that it is addressed to pupils who are not taking science as a major subject. Many schools now require pupils specializing in the humanities to take some kind of science course for a limited period. This can be done in a number of ways. Some teachers treat a narrow field in depththe subjects of atomic and nuclear physics are often selected for this approach. Others atttempt courses on the history and methods of science. The author of this article describes a third method. He discusses the chemistry of a number of substances which are familiar to students in their everyday life and he has collected together a number of interesting experiments which illustrate some industrial organic reactions. (The experiment on putting out a paraffin fire with paraffin, while undoubtedly spectacular, is perhaps one which might be omitted.) The topics discussed include fuels, soaps and detergents, esters, polymers, dyes, etc., and there are useful details of the way in which the practical work is organized and the type of instruction sheet issued to the pupils.

A number of articles on industrial processes at a level suitable for use in schools have appeared in recent years for which there is unfortunately no room in the present volume. An interesting article in the inorganic field is on "The Structure and Manufacture of Porcelain" by W. Flörke (Der Mathematische und Naturwissenschaftliche Unterricht, vol. 19, 1966-1967, p. 342). The applied chemistry of this substance which most people handle everyday of their lives correlates a great deal of fundamental inorganic chemistry in a relatively simple structural framework. Details of the synthetic ammonia industry in the United States are given in an "Industry Profile" (Chemistry, vol. 39, no. 6, 1966, p. 14). The hydrogen in this case is obtained by the catalytic steam reforming of natural gas. "Le Fluor" by J. Robin (Bulletin de l'Union des Physiciens, No. 495, 1967, p. 425) discusses the laboratory and industrial preparation of fluorine and some of the important fluorine compounds now made on the industrial

Paper is another common substance rarely discussed in school textbooks and courses. An article by H. Corte entitled "Fundamental Properties of Paper" (School Science Review, No. 162, 1966, p. 331) contains much interesting detail on cellulose chemistry.

d'étudier séparément la fabrication industrielle d'un grand nombre de substances. C'est ainsi qu'il examine successivement, en fournissant des exemples appropriés, l'hydrogénation et la déshydrogénation, l'hydratation, la chloruration, l'alkylation, l'estérification, l'oxydation, l'isomérisation et la polymérisation. La chimie industrielle ne doit pas être enseignée comme une matière séparée, et ces exemples industriels peuvent être introduits dans le cours au moment voulu.

L'article de T. C. Swinfen diffère des autres articles contenus dans ce volume en ce qu'il s'adresse à des élèves pour lesquels les sciences ne constituent pas une matière principale. De nombreuses écoles obligent maintenant les élèves qui se spécialisent dans les lettres à suivre pendant un certain temps un cours scientifique. Cela peut se faire de plusieurs façons. Certains enseignants traitent de façon approfondie un domaine limité, la physique atomique et nucléaire étant souvent choisie à cet effet. D'autres font un cours sur l'histoire de la science et les méthodes scientifiques. L'auteur du présent article décrit une troisième méthode. Il étudie la chimie de plusieurs substances que les élèves rencontrent couramment dans la vie quotidienne et il a réuni un certain nombre d'expériences intéressantes qui illustrent certaines réactions organiques industrielles (on peut omettre l'expérience qui consiste à éteindre un feu de paraffine avec de la paraffine malgré son caractère spectaculaire). Parmi les sujets traités figurent les pétroles, les savons et les détergents, les esters, les polymères, les teintures, etc., et des détails utiles sont donnés sur la façon d'organiser le travail pratique et sur les feuilles d'instructions qui sont données aux élèves.

Ces dernières années ont paru plusieurs articles relatifs à des procédés industriels, d'un niveau convenant à une utilisation scolaire, mais il n'a malheureusement pas été possible. faute de place, de les faire figurer dans le présent volume. Dans le domaine de la chimie minérale, un article intéressant est celui consacré à « La structure et la fabrication de la porcelaine », de W. Flörke (Der Mathematische und Naturwissenschaftliche Unterricht, vol. 19, 1966-1967, p. 342). La chimie appliquée de cette substance que la plupart des gens utilisent quotidiennement met en jeu de nombreuses notions fondament a les de chimie minérale à l'intention d'un cadre structurel assez simple. On trouvera des renseignements sur l'industrie de l'ammoniac synthétique aux États-Unis dans un article de la série « Industry profile » (Chemistry, vol. 39, nº 6, 1966, p. 14). Dans ce cas, l'hydrogène est obtenu par la régénération catalytique à la vapeur du gaz naturel. J. Robin dans « Le fluor » (Bulletin de l'Union des physiciens. nº 495, 1967, p. 425) examine la préparation de ce corps en laboratoire et dans l'industrie, ainsi que celle de certains composés importants du fluor qui sont maintenant fabriqués à l'échelle industrielle.

Le papier est une autre substance courante qui est rarement étudiée dans les manuels et les cours scolaires. Un article de H. Corte, intitulé «Fundamental properties of paper» (School science review, no 162, 1966, p. 331) contient de nombreux détails intéressants sur la chimie de la cellulose.

METHODOLOGY OF APPLIED CHEMISTRY TEACHING IN ADVANCED SCHOOL COURSES

by A.M. Neimark, A.A. Sundarkin and D.A. Apshtain

The involvement of chemistry with the national economy is proceeding in this country and a number of chemical plants are under construction which are going to be equipped with modern facilities.

Chemicals are used in various branches of industry and agriculture and the involvement of chemistry with the national economy requires a great number of qualified persons for work in chemical laboratories and in industry.

Secondary school education is a minimum background for these persons and their professional training should be based on a broad, technical and academic foundation.

The training of pupils at the secondary school should be conducted in a way which will provide them with some preliminary understanding of the work involved in the practical applications of chemistry and which in itself will assist graduates to master the profession and learn chemistry more easily. It is known that pupils in Form VIII show great interest in chemistry and one could form special chemistry classes in Form IX for these students.

The ideal of teaching is to foster the interest of older pupils in the profession of chemistry. This can only be achieved if the educational method reinforces the knowledge and skill which the pupils obtain in general subjects and in a deeper study of chemistry.

Actually in practical teaching one must steadily strive to inter-relate theory and practical work. This practical teaching includes subjects which give pupils a wide background of industrial chemical knowledge and skills. The elements of chemical analysis and chemical technology are among these subjects. The Ministry of Education has adopted a plan for the practical teaching of applied chemistry in the 1966/67 school year based on these principles (see Table 1).

The subject 'Elements of Chemical Analysis' trains pupils in the skills needed in any industrial, academic, agrochemical, or

pharmaceutical laboratory and in many other branches of industry as well. It consists of the following sections: laboratory technique, qualitative analysis, quantitative analysis, instrumental methods of analysis. Pupils learn the technique of laboratory work, cleaning of glassware, construction of simple glass apparatus, weighing, preparation of solutions of weight and volume concentration etc.

TABLE I

Time needed (in hours) for practical teaching in applied chemistry

Subjects			Nur	mber of F	Periods		
	per v Term I	Class IX week Term II	per year	1945 C	Class X week l Term II	oer year	Total
Elements of Analysis	4	4	140	2	2	70	210
Elements of Technology	(-	=	.=	2	2	70	70
Practical Work	» -	-	144	_	_	_	144

In the Elements of analysis course the pupils carry out qualitative analysis of cations and anions. They should be taught to use an analytical balance. At first they spend a great deal of time on weighing and teachers should give this special attention. The principles of gravimetric analysis are then discussed.

Volumetric analysis is preceded by a lesson devoted to calculations on molar and normal concentrations. Pupils become familiar with indicators in neutralization reactions. Oxidation and reduction is studied by constructing equations for oxidation and reduction reactions, first for simple substances and then for more complex ones. Permanganimetric and iodimetric methods are then discussed. Pupils should know why the permanganate reaction is carried out in acid solution and they should understand the structure of sodium thiosulphate and the chemical reaction it undergoes with

The choice of other methods of analysis is determined by the capabilities of the laboratory and the requirements of the practical course. Instrumental methods such as colorimetric analysis, potentiometry, electrolysis, chromatography etc. are widely used in scientific laboratories at the present time. Students get acquainted with these methods by studying the theory after which they study the design of apparatus and carry out appropriate experiments.

The topic 'Elements of Chemical Analysis' has an important role to play in getting students interested in chemistry and its practical applications. Pupils develop certain skills which enable them to apply their theoretical knowledge in everyday life.

The content of the special analysis course is determined by the type of factory laboratory in which the industrial education course is carried out. Thus pupils in the chemistry classes of school no. 710 get acquainted with photoelectrocolorimetric and potentiometric control methods. Special attention must be directed to the chemical basis of the methods and the calculations involved. Work on the analysis of aromatic amines, nitrocompounds and sulphoxides has been carried out. Pupils get a firm idea of auxochromic and chromophor groups and thus improve their knowledge of organic chemistry. All this work is carried out by the pupils in the Dorogomilov plant laboratory which is equipped with photoelectric colorimetric and potentiometric instruments.

An original course in special analysis can be developed on the basis of the pharmacist's shop. The students first get acquainted with physical methods of analysis. Then they determine solubilities according to the schemes given in the government pharmacopoeia. They become familiar with methods of analysis (both inorganic and organic) for certain groups of reactions.

Chemistry students study 'The basis of chemical technology' in Class X. The general chemistry course in secondary schools discusses the most important problems of the national economy - metallurgy, chemistry in agriculture, organic syntheses based on natural gas, etc. All pupils must be familiar with this since it is an important element in industrial education. However, the general chemistry syllabus does not contain sufficient chemical technology. The topic 'Basis of chemical technology' is therefore taught as a separate subject in chemistry courses. General principles of chemical industry (mechanisation, electrification, automisation etc.) are included in the syllabus. There are only 70 periods available

so the teaching has to be very efficient. The course is not an easy one and maximum effort must be applied to get pupils interested in it, with the assistance of various aids - models, slides, films etc. It is very important that students should become acquainted with local chemical plants. Their ideas on the general bases of chemical technology are developed in 1 - 6 periods spent in the factory for this purpose.

If the pupils can assist the factory and the head of the laboratory good relationships are established and this has a good educational effect. They get acquainted with working conditions, safety precautions, methods of production which they can relate to their theoretical studies and the knowledge they have obtained from the course on analysis. They refresh their skill at using analytical balances, preparing solutions and obtain new information about control methods.

Some students in Moscow school No. 62 had their industrial practice in the pharmaceutical faculty of the First Moscow Medical Institute. All the pupils worked with enthusiasm and got good results.

If students practical work is carried out in agriculture they have to have a different course in which they are taught theoretical and practical agricultural chemistry. Time for this can be taken from the 'Basis of chemical technology' course. The timetable for the agricultural course is as follows:

TABLE 2

Periods per week for chemistry classes in agricultural courses.

		ar bcb.		
Subject	Class Term I	IX Term II	Class Term 1	3 X
Foundations of chemical analysis	4	2		Term II
Foundations of plant growth	_	2	2	-
Foundations of agrochemistry	-	~	-	-
			2	4

The short course 'Foundations of plant growth' has to be given as an introduction to the course on agrochemistry.

Pupils get acquainted with the agrochemical properties of soil, with methods of using fertilisers, methods of plant cultivation and they do practical work on these topics. The theoretical and practical knowledge they obtain is then used during their agricultural practice. The course on 'Foundations of agrochemistry' includes topics such as biology, industrial education and the foundations of chemical analysis. Special attention must be paid to methods such as the determination of pH, determination of nitrogen, phosphorus, potassium and the quality of crops. Physical and chemical methods of analysis are recommended: colorimetry, potentiometry, flame photometry, refractometry etc.

If pupils wish to have professional training they will be given it according to the needs of the national economy. In these cases they will receive an extra course (2 periods per week in Classes IX and X) which will give them the necessary knowledge and skills for the profession.

Good results have been obtained from practical work by pupils in pharmacies. The main purpose of this practice is to develop the pupils interest in chemistry and especially biochemistry. The general chemistry course and the foundations of chemical analysis are widely studied in these classes. There are certain changes in the syllabus of the course in chemical analysis. Questions of chemical technology are studied in the general chemistry course, and instead of the Chemical Technology course they study the 'Foundations of Pharmaceutical Chemistry'. The technology and the preparation of drugs are studied in the course, as is Latin. They are taught pharmaceutical technology during their practical course in the pharmacies.

If students have a practical course at a metallurgical plant the course on chemical technology should be replaced by one on the 'Foundations of Metallurgy'.

Experience has shown that these courses can be implemented quite successfully by the joint efforts of school and industry. The course on analysis is given by the schoolteacher, but special topics on analysis and technology can be taught by experts from industry.



THE PHYSICAL CHEMISTRY OF AMMONIA MANUFACTURE AND NITROGENOUS FERTILIZER PRODUCTION

By J. T. Gallagher, B.Sc., Ph.D. and F. M. Tayler, B.Sc., Ph.D., F.R.I.C. ICI, Agricultural Division, Billingham, Co. Durham

The synthetic ammonia industry, although still young in comparison with most other branches of the heavy chemical industry, has rapidly risen to a position of great importance due almost entirely to the everincreasing demands for fertilizers. annual consumption of the three main fertilizer nutrients, nitrogen, phosphate and potash has grown from about three million tons at the end of the first decade of this century to currently over thirty million tons. During the last ten years the rate of increase in nitrogen fertilizer consumption in particular has accelerated. These facts are clearly demonstrated in Fig. 1. Bearing in mind the need to raise living standards in many countries, the rising standards in others, and the current 'explosion' in world population, a continuation in the growth of fertilizer consumption is certain. As one may imagine, the industrial processes involved in ammonia synthesis and fertilizer production are both numerous and complex. To describe the whole in detail would require much more space than is possible here. It is intended to emphasize in this article some of the basic chemistry and physico-chemical principles involved in the major steps only.

The 'chemical story' we wish to relate starts with hydrogen in natural hydrocarbons (e.g. petroleum 'light ends' or natural gas) and nitrogen in the air. It is the task of the industrial chemist to create an efficient chemical pathway forward to the nitrogencontaining fertilizers. The basic steps along this route are shown in Fig. 2. First, the hydrogen in the raw material must be liberated for its subsequent use in the fixation of atmospheric nitrogen as ammonia. The next step is to convert this ammonia into compounds which are suitable for application to the soil; at the present time there are three principal ways of doing this.

One method, and probably the most important, consists of oxidizing some ammonia to nitric acid and neutralizing this with a further quantity of ammonia to give ammonium nitrate. In another, the ammonia is converted into urea by reaction with carbon dioxide under pressure. In the third method ammonia is converted to its sulphate by direct neutralization or by reaction with carbon dioxide followed by a double decomposition with calcium sulphate.

Our main aim is to show how the principles of thermodynamics and kinetics dominate the industrial chemistry of these processes. Although it is the second step in the sequence, ammonia synthesis is a clear, well-known example of the application of these principles and will therefore be considered first.

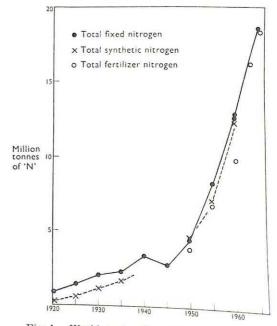


Fig. 1. World production of 'fixed' nitrogen.

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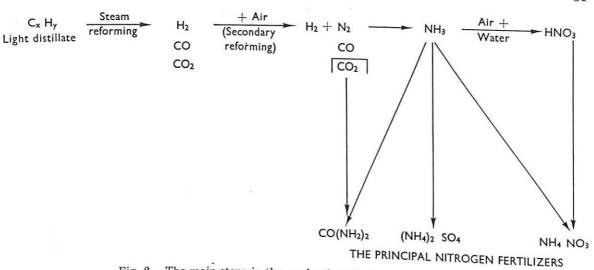


Fig. 2. The main steps in the production of nitrogen fertilizers.

THE SYNTHESIS OF AMMONIA

For more than a century following the discovery of ammonia and its chemical composition, efforts were made to produce the compound by combining the stoichiometric quantities of hydrogen and nitrogen. At first regarded as an academic puzzle, the problem acquired great industrial importance after Leibig demonstrated that ammoniacontaining fertilizers can boost yields of agricultural crops. The catalytic synthesis of ammonia from its elements was subsequently accomplished during the early years of the twentieth century by Haber and his co-workers.

The essential process is the exothermic reaction

 $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(Heat evolved = $13.0 \text{ kcal/mole NH}_3 \text{ at } 500^{\circ}\text{C*}$)

which is very slow at all normal temperatures in the absence of a catalyst. Being reversible, the reaction does not go to completion even in the presence of a catalyst. In fact, an equilibrium is set up in which the concentration of the reactants is appreciable.

The application of Le Chatelier's principle

*The heat evolved or absorbed in a chemical reaction varies with the temperature of reaction. The value quoted here is for a temperature of 500°C since, as is explained later, this is a typical reaction temperature used in industrial plants. Often, however, the reaction heat is quoted at a standard temperature of 25°C. This practice is followed throughout the rest of the article.

to this reaction shows that qualitatively, the concentration of ammonia at equilibrium is increased either by an increase in total pressure or a decrease in temperature. To the industrial chemist, however, qualitative information is not sufficient; he must have a knowledge of the quantitative effects of these two variables. By the application of well-known chemical laws and equations this can be accomplished.

Thus, the quantitative effect of temperature is expressed by the well-known van't Hoff isochore.

$$\mathrm{dln}\ K/\mathrm{d}T\ = \Delta H/\mathbf{R}T^2$$

where K is the equilibrium constant at temperature, T, ΔH is the heat of reaction and R is the gas constant.

The quantitative effect of pressure at a given temperature is governed by other familiar laws. For a reversible reaction, equilibrium constants are derived from the law of mass action. In this case

$$K\,=\,(P_{\rm NH_3})^2/(P_{\rm H_2})^3P_{\rm N_2}$$

where P_x = partial pressure of component x. In fact, at high pressures this equation must be modified to

$$K = (f_{\rm NH_3})^2/(f_{\rm H_2})^3 (f_{\rm N_2})$$

where f_x is known as the fugacity of component x. This parameter is introduced to correct for deviations from the perfect gas

laws at higher pressures. Such deviations can be quite large, about 20 per cent for $\rm H_2$ and $\rm N_2$ at 350 atm pressure. Fugacity values are calculated from modified gas equations of state, and experimental pressure, volume and temperature data.

In this way the equilibrium concentrations of N_2 , H_2 , and NH_3 can be calculated over derived pressure and temperature ranges. It is important to realize that knowledge of these equilibria is essential before any understanding of synthesis conditions is possible. Examples of the concentration of ammonia in equilibrium with a 3:1 mixture of H_2 and N_2 are given in Fig. 3. It is clear

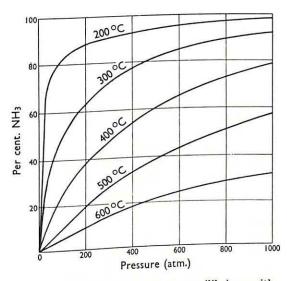


Fig. 3. Percentage ammonia in equilibrium with $3H_2:1N_2$ mixture.

that since the equilibrium concentration of ammonia is considerably greater at lower temperatures, a low synthesis temperature is desirable. However, at these low temperatures the *rate* of synthesis is impracticably low, and only increases as the temperature is raised, according to the well-known Arrhenius equation:

$$d\ln k/dT = \Delta E/RT^2$$

where k is the velocity constant at temperature T, and ΔE is a parameter called the activation energy.

This conflict between the demands for high temperature to produce high reaction rates and low temperatures to ensure high equilibrium product concentrations often occurs in chemical systems. The problem is resolved in this case by the introduction of iron catalysts which can increase the reaction rates at the lower temperatures without affecting the position of equilibrium. No such conflict exists with the pressure; an increase improves both reaction rates and the equilibrium position.

Most modern ammonia plants operate at about 150–350 atm in the temperature range 350–600°C. Below these temperatures the catalyst loses its activity. Clearly the discovery of a more active catalyst, *i.e.* one which can induce commercially acceptable rates at even lower temperatures, could revolutionise the whole process. This problem is not easy, however, and despite the great efforts devoted to its solution, improvements in the early ammonia synthesis catalyst have been of a relatively minor nature.

Reference to Fig. 3 shows that most plants operate under conditions corresponding to ammonia equilibrium concentrations in the range 15-50 per cent. The gases are continually passed through the catalyst bed at such rates that they do not reach these equilibrium values during their 'contact time': indeed, only a small fraction of the reactants are converted. Such rates are employed since the actual production of ammonia (which is equal to the product of the 'fractional conversion' and the quantity of reactants passed in a given time) is found to rise to a limiting value at higher flow rates. The attainment of equilibrium conversions corresponds to low productions since it is only possible at low flow rates, as illustrated in Fig. 4. For reasons of economy, the ammonia is condensed out of the gas stream and the unreacted hydrogen and nitrogen are recirculated continually, fresh make-up gas being added as fast as ammonia is removed. A more detailed account of the synthesis process is given in a booklet Ammonia—Manufacture and Uses by A. J. Harding, published by Oxford University Press.

GAS MAKING IN AMMONIA SYNTHESIS—THE HYDROGEN SOURCES

There are two main steps in synthetic ammonia production—the preparation of hydrogen and the reaction between hydrogen and nitrogen (in abundant supply from the air) to form ammonia. It is the former which now controls the economics of the whole process.

There are four main sources of hydrogen: water, natural gas, coal and oil, and a number of techniques have been devised for its isolation. In some processes the combustion of a fuel provides energy necessary to release the hydrogen from water. This is the largely obsolescent water-gas generation technique.

$$C + H_2O \rightleftharpoons CO + H_2$$
(Heat absorbed = 31·4 kcal/mole at 25°C)

In other cases, no water is used and the fuel is the sole source of hydrogen; this occurs in the partial combustion of natural gases.

$$\begin{array}{c} e.g.~\mathrm{CH_4}~+~\frac{1}{2}\mathrm{O_2}~\rightleftarrows~\mathrm{CO}~+~2\mathrm{H_2}\\ \mathrm{(Heat~evolved}~=~8.5~\mathrm{kcal/mole~at~25^{\circ}C)} \end{array}$$

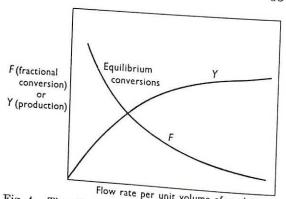
In a third process, hydrogen is derived from both fuel and water simultaneously, as in the steam reforming of natural gas, or light distillate fractions of petroleum.

e.g.
$$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$$

(Heat absorbed = $49 \cdot 3 \text{ kcal/mole at } 25^{\circ}\text{C}$)

$$C_2H_6 + 2H_2O \rightleftharpoons 2CO + 5H_2$$
(Heat absorbed = 83.0 kcal/mole at 25°C)

Great changes in the relative importance of these three types of process have occurred over the last twenty years. Until 1939 about 90 per cent of the hydrogen was made from coke and steam through the water-gas reaction. Since that time advantage was made of the existence of cheap and plentiful supplies of natural gas and oil in certain countries, for example, the U.S.A. and Italy. The economic superiority of processes using these sources, coupled with the steady increase in coal costs, threatened the manufacture of hydrogen in the United Kingdom and other countries where little natural gas



Flow rate per unit volume of catalyst

Fig. 4. The effect of flow rate on (a) the fractional conversion of reactant gases passed and (b) the total

During the 1950's intensive research was carried out in order to meet this challenge. One cheap feedstock was available in quantity in this country—light distillate, the sulphurcontaining low-boiling fraction from petroleum refineries. Steam reforming of light distillate was not a new idea in itself—it had been accomplished at atmospheric pressures as early as 1938. The problem was to operate at higher pressures thus effecting substantial savings in the cost of compressing synthesis gas. Certain technical problems were involved in desulphurizing light distillate and continuously reforming it at pressure, including the problem of finding materials for reformer-tube construction capable of withextremes of temperature and pressure. Since the process was also catalytic, a robust catalyst had to be developed which did not deteriorate when subjected to the severe thermal and mechanical stresses existing under reaction conditions. Furthermore, at high temperature and pressure, thermal cracking of light distillate occurs, depositing carbon; this reaction occurs at the catalyst surface and the elementary carbon thus formed causes a physical blocking of the surface which in turn produces deactivation. This undesirable side reaction had to be effectively limited.

By 1959, answers to these difficulties had been found. Three years later the chemical industry was able to introduce the pressure steam reforming process on a full commercial scale. The new process transformed the economics of producing ammonia and allied chemicals based on hydrogen in

countries without natural gas. The production and capital investment costs in the United Kingdom, for example, are about 47 per cent and 30 per cent of those incurred in the water gas process. The success of the new process is mirrored in the trend towards the new raw material source as shown in Fig. 5.

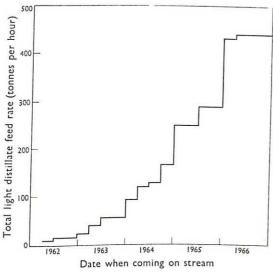
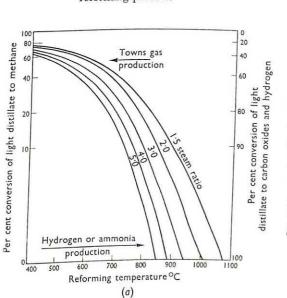


Fig. 5. The reforming capacity for all purposes. either in operation or construction, using the steam reforming process.

in the production of hydrogen for ammonia cent conversion of light distillate to methane 20 Towns gas distillate to carbon oxides and hydrogen production distillate to carbon oxides and hydrogen Per cent conversion of light Per cent conversion of Per 30 Reforming pressure (atm.) (b)



The effect of steam ratio and reforming temperature on the equilibrium conversion of Fig. 6(a). The effect of steam ratio and reforming pressure on the equilibrium conversion of light distillate at 10 atm pressure. (b). The effect of steam ratio and reforming pressure on the equilibrium conversion of light distillate at 700°C.

The chemistry involves the reaction of lower paraffins with steam over a nickelbased catalyst. The gases, at 650-800°C and 10-25 atm pressure, are continually passed through a reformer tube packed with catalyst. In contrast to ammonia synthesis, the reaction between light distillate and steam can produce a range of product gas compositions, depending upon the operating conditions. The factors involved can be readily understood by reference to Figs. 6(a) and 6(b) which show the effect of pressure and temperature and the so-called 'steam ratio' (the ratio of moles of steam to atoms of carbon in the feed gas of the reformer) upon the composition of the product gases. Here again a knowledge of equilibrium conditions can guide the industrial chemist to the optimum operating conditions. The equilibria obtained at very high temperature, low pressure and high steam ratios correspond to a complete reforming of the light distillate to give carbon oxides and hydrogen. At the other extreme a product gas with virtually no hydrogen present, in which the maximum amount of carbon is reformed to methane, is produced at very low temperatures, high pressures, and low steam ratios. Clearly,

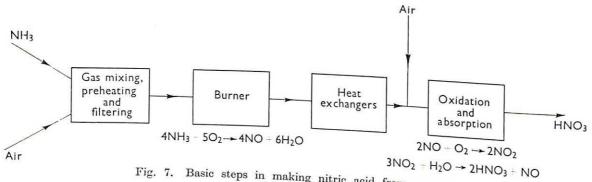


Fig. 7. Basic steps in making nitric acid from ammonia.

synthesis the former conditions are employed.*

Here, in contrast to the ammonia synthesis, any conflict between favourable reaction rates and equilibria involves the pressure and not the temperature of operation. Rates are greater at high pressures, but equilibria are not quite so favourable; high temperatures are favourable from both points of view. There are, however, other factors to be considered which impose limitations upon final operating conditions. These include materials of reformer tube construction, the physical strength of the catalyst and the carbon laydown problem, all referred to earlier

NITROGENOUS FERTILIZERS

Referring to Fig. 2 we see that the ammonia is mainly used to finally make ammonium nitrate, urea and ammonium sulphate, three of the principal nitrogenous fertilizers. Ammonium sulphate, having the lowest nitrogen content, is tending to fall out of favour, because it is a relatively expensive way of transporting nitrogen and distributing it on the fields. Fertilizers based on ammonium nitrate and urea are more economic because of their high nitrogen analyses, but there are some agronomic difficulties, yet to be overcome, in the use of urea in some conditions in temperate

climates. We will look in detail at nitric acid (an intermediate in the sequence) and urea manufacture, while only briefly at the processes used to make ammonium sulphate

NITRIC ACID

The conversion of ammonia to nitric acid is an excellent example of the interplay of kinetic and equilibrium factors in industrial processes. It takes place in two stages. The first of these is the catalytic oxidation of ammonia to nitric oxide at high temperature according to the overall equation

$$4\mathrm{NH_3} + 5\mathrm{O_2} \rightleftharpoons 4\mathrm{NO} + 6\mathrm{H_2O}$$
(Heat evolved = $216.2 \mathrm{\ kcal/mole\ at\ } 25^{\circ}\mathrm{C}$)

The second stage is the gas phase oxidation of nitrie oxide to nitrogen dioxide and the subsequent absorption of the latter in water.

$$2NO + O_2 \rightleftharpoons 2NO_2$$
 (Heat evolved = 26.9 kcal/mole at 25° C)

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$$
(Heat evolved = $27.7 \text{ kcal/mole at } 25^{\circ}\text{C}$)
the plant consists of few

The plant consists of four main sections (Fig. 7). In order to avoid danger of explosions in the catalyst chamber (or burner), special precautions are taken in the gas-mixing part of the plant to produce mixtures of air and ammonia outside explosive limits. The gases are also filtered here in order to remove solid material such as iron oxides, which may interfere with the operation of the catalyst.

The main oxidation reaction takes place on a gauze pad of platinum-rhodium alloy in the temperature range 700-900°C. At

^{*} It is of interest in passing to note that the steam reforming of light distillate under the latter condition can be adapted to other process requirements, in particular, the production of town gas. Indeed, the steam reforming process is already established as a reliable and low capital cost method of producing town gas.

this temperature and at atmospheric pressure, the equilibrium of the system favours the formation of elementary nitrogen, practically to the exclusion of the alternative product, nitrie oxide.

$$4NH_3 + 3O_2 \approx 2N_2 + 6H_2O$$

The problem of obtaining a high yield of nitric oxide is therefore one of kinetics, that is to find a catalyst and reaction conditions which will promote the formation of nitric oxide and suppress side reactions leading to nitrous oxide or elementary nitrogen. This problem of how to stop a reaction at the stage of high yield of a required product before it progresses to the equilibrium state, at which the yield of the desired product is low, is of a type often encountered in the chemical industry.*

The temperature range of 800-900°C is chosen since it is only in this range that commercially acceptable rates of oxidation occur. The gas flow rate is critical; under optimum conditions a very high conversion of ammonia to nitric oxide occurs. However, if it is too high, some ammonia passes unconverted through the gauze thence to take part in a rapid gas-phase reaction with nitric oxide, producing elementary nitrogen

$$4NH_3 + 6NO \Rightarrow 5N_2 + 6H_2O$$

On the other hand, it has been clearly demonstrated that nitric oxide is rapidly decomposed on a platimum catalyst at 800-900°C, the rate of dissociation increasing markedly with temperature. Thus, if the linear gas flow across the gauze is too slow, dissociation of nitric oxide to its elements takes place.

There is, therefore, for a given catalyst arrangement, an optimum condition of gas rate, gas composition and gauze temperature for maximum conversion of ammonia

* Another example of this state of affairs is the catalytic oxidation of methanol to formaldehyde. The thermodynamic equilibrium of this system lies at large concentrations of carbon dioxide and water, but by the application of certain reaction conditions a high conversion of methanol to formaldehyde is obtained. The catalytic hydrogenation of carbon monoxide to methanol provides another illustration. The equilibrium in this system favours the production of methane but by suitable choice of catalyst and reaction conditions, high yields of methanol may be obtained.

to nitric oxide. Fortunately this optimum is found to be rather wide in practice, linear gas flow rates between one and three feet per second having been used on various plants which have operated at high efficiency.

Whereas in the ammonia burner the kinetics of the reaction are the dominant consideration, in the absorption section both kinetic and equilibrium considerations are important. There are two reactions to be considered here, the gas-phase oxidation of nitric oxide to nitrogen dioxide and the absorption of nitrogen dioxide in water. The equations are shown above. These in fact are closely interlinked because the absorption of nitrogen dioxide liberates nitric oxide which must be re-oxidized before it can be absorbed. However, they will be discussed separately.

The oxidation of nitric oxide to nitrogen dioxide has a negative temperature coefficient, a point of great importance in nitric acid practice. The reaction only becomes reasonably quick at temperatures under 30°C; consequently good cooling of the gases in the heat exchangers will assist in speeding up the reaction. Furthermore. it is of the third order and its rate is therefore very slow at low partial pressures of the reactants. In order to achieve reasonably complete reaction in the absorption towers, the gases must either be compressed at some earlier stage, or the towers must be sufficiently large to allow the gases a long residence time. In this way the kinetics of the reaction determine the size of the absorption towers.

No kinetic problem is faced with the absorption process. The reaction is sufficiently rapid at ordinary temperatures to achieve the equilibrium state. The equilibrium constant can be written in the usual fashion.

$$K = (P_{\text{HNO}_3})^2 . P_{\text{NO}} / (P_{\text{NO}_2})^3 . P_{\text{H}_2\text{O}}$$

It is clear from a simple application of Le Chatelier's principle to the above equilibrium that the higher the pressure and the higher the ratio of NO₂:NO, the greater will be the concentration of the acid produced. Thus the overall pressure of the system influences the kinetics of one reaction and the equilibrium position of another.

In practice the production at 60 per cent nitric acid requires an operating pressure of 8 atm, while 50 per cent acid is obtained by operating at 1 atm.

UREA SYNTHESIS

Urea is a very concentrated source of nitrogen, containing 46 per cent by weight compared with, say, ammonium sulphate (21 per cent) or ammonium nitrate (35 per cent). It is synthesized industrially by reacting carbon dioxide with ammonia in pressure vessels and extracting the product continually in the molten state.

Compared to the processes already described, the synthesis of urea is more effectively dominated by equilibrium considerations, the reactions involved being fast and needing no catalysis. Two important consecutive reactions occur:

 $\begin{array}{l} 2{\rm NH_3} \,+\, {\rm CO_2} \, \rightleftharpoons \, {\rm NH_4OCONH_2} \\ ({\rm Heat~evolved} \,=\, 38{\cdot}1 \,\, {\rm kcal/mole~at~25^{\circ}C}) \end{array}$

 $\mathrm{NH_4OCONH_2} \rightleftharpoons \mathrm{CO(NH_2)_2} + \mathrm{H_2O}$ (Heat absorbed = 6.8 kcal/mole at $25^{\circ}\mathrm{C}$)

The first stage, formation of ammonium carbamate, is exothermic and there is the consequent risk that the temperature will rise causing dissociation unless the process is kept above its dissociation pressure. For this reason, and also in accord with Le Chatelier's principle, the reaction is conducted at high pressures. The rate of formation of carbamate is found to be proportional to the square of the pressure and consequently its formation under typical operating conditions of 200 atm and 190°C is practically instantaneous; hence the first stage can be regarded as being always at equilibrium.

The rate of conversion of carbamate to urea is also quite fast under these conditions so that even at short residence times in a reactor the equilibrium conditions for this second step can be approached. A typical yield from a urea converter would be about 90 per cent of the equilibrium conversion.

One point of particular interest is that the equilibrium conversions are extremely sensitive to the ammonia concentrations. For example, at about 150°C, using stoichiometric ratios of ammonia and carbon

dioxide, the equilibrium lies at 40 per cent conversion. If an excess of say $1\frac{1}{3}$ of the required amount of ammonia is added, however, the equilibrium in the system lies at about 75 per cent conversion. This shift in the equilibrium produced by adding the excess ammonia is greater than that calculated from the simple equilibrium according to the second equation above. It can only be explained by invoking more advanced theories on the activity of reacting species in a chemical reaction—rather like the fugacities of non-ideal gases mentioned earlier. Such theories are outside the scope of this article. Ammonia excesses of the above-mentioned order are, however, often used, either being recycled to the process, or passed to other ammonia-using processes.

There is at least one other reaction of importance which occurs in the reactor. This involves the formation of a compound called biuret.

 $2(\mathrm{NH_2})_2\mathrm{CO} \rightarrow \mathrm{NH_3} + \mathrm{NH_2}\mathrm{CONHCONH_2}$ This is a relatively slow step and is suppressed both in rate and equilibrium by the excess ammonia in the system. It is indeed of vital importance that the biuret content of the product is maintained below 1 per cent since this impurity can inhibit plant growth.

AMMONIUM NITRATE

The physical chemistry of the manufacture of both ammonium nitrate and ammonium sulphate is of less interest than the processes described in detail earlier. The only commercial processes for the manufacture of the former are based on the reaction between ammonia and nitric acid. The neutralization is typical of reactions between a strong acid and strong base, i.e. it is extremely rapid, goes virtually to completion and evolves considerable quantities of heat. Indeed, the heat of reaction is used to evaporate much of the water from the system to produce highly concentrated solutions or 'melts', from which granular ammonium nitrate is formed by spraying the melt down a tower.

An alternative form of ammonium nitrate fertilizer is produced by mixing the concentrated ammonium nitrate solutions with

ground limestone or chalk in such a fashion that the product agglomerates into acceptable granular form.

AMMONIUM SULPHATE

This is made in two principal ways, the direct neutralization of sulphuric acid with gaseous ammonia (a process very similar to ammonium nitrate production) or by the double decomposition of calcium sulphate with ammonium carbonate solution.

In the former process the heat of reaction is again used to boil off water from the system, thus producing a saturated solution solution. After several hours the product, calcium carbonate, is removed by filtration and the filtrate is evaporated to yield crystalline ammonium sulphate.

SUMMARY

The principal objective of this article has been to illustrate how the manufacturing steps in nitrogen fixation and the conversion of ammonia to fertilizer are dominated by basic physical chemistry, *i.e.* both the thermo-dynamics and kinetics of the processes. The chemist manipulates these to make the products in high yield. We might summarize this in the following Table:

REACTION	FACTORS DETERMINING MANUFACTURING METHOD	FACTORS DETERMINING HIGH YIELDS 1. Catalyst lowers reaction temperature. 2. High pressure improves equilibrium yield. 3. Recycle unused N ₂ and H ₂ . 1. Selective catalyst to avoid carbon formation. 2. High temperature and excess steam to give favourable equilibria.		
$\rm N_2+3H_2 \rightleftharpoons 2NH_3$	Slow kinetics demand high reaction temperature which adversely affects equilibrium.			
$C_{n}H_{2}n_{+2} + nH_{2}O \rightleftharpoons $ $nCO + (4n + 2)H_{2}$	High pressures are needed for economic reasons; this helps the kinetics but gives more unfavourable equilibrium. Side reactions produce carbon which fouls the catalyst.			
$4\mathrm{NH_3}+5\mathrm{O_2} \rightleftharpoons 4\mathrm{NO}+6\mathrm{H_2O}$	Equilibrium favours N ₂ formation.	Very fast catalytic reaction gives NO, which is passed quickly from the reactor, so that N ₂ formation is avoided.		
(1) $2NO + O_2 \rightleftharpoons 2NO_2$ (2) $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$	Size of absorption towers influenced by kinetics of (1). Strength of acid influenced by equilibrium of (2).	High pressure speeds up (1) and gives more favourable equilibrium of (2).		
$2NH_3 + CO \rightleftharpoons$ $CO(NH_2)_2 + H_2O$	Mainly limited by equilibrium conversion.	High pressure and excess of ammonia give favourable equilibrium conversion.		

containing crystals of sulphate. By careful design of the reactor and crystal removal device, crystals of a required size can be produced. The wet crystals are centrifuged to remove excess mother liquor and finally transferred to a rotary drier.

In the second manufacturing technique ammonium carbonate solution is produced by dissolution of anhydrous ammonia and carbon dioxide, generally at high pressure. By careful temperature control a somewhat unstable product is obtained. The heated solution is then reacted with finely ground calcium sulphate. This reaction is relatively slow, the rate being dependent on accessability of the solid surface to the reactant

It has been possible to describe only the broader aspects which govern the work of the industrial physical chemist. Inside the framework of the fertilizer industry alone, there remain many opportunities for technological advances, and a constant search is carried out to achieve such improvements. Because of the large scale of operation of the processes described, small technical gains can mean very large economic gains. Behind all such technical and economic incentives to the industrial scientist and engineer there remains, however, the most important one of all—that he is making a very great contribution to meeting the problem of world hunger.



THE POLYTECHNIC PRINCIPLE IN TEACHING ORGANIC CHEMISTRY

by L.A. Koozyrev

The 'polytechnic principle' means the inclusion of appropriate industrial material in the syllabus of the basic sciences to help pupils to gain some knowledge of the main branches of industry, to develop their abilities and skills in using tools, and to educate their creative thinking and general industrial culture.

However, the polytechnic principle of teaching is not a detailed study of particular branches of industry; it only means a study of the fundamental principles of modern industry. What are the common characteristics of many branches of the chemical industry? Analysis shows that common features are typical chemical reactions, typical apparatus, control methods, principles of organisation of chemical industry and development trends in chemical technology. In this paper we shall discuss typical reactions in the organic chemistry industry. During their studies in inorganic chemistry pupils have come across many reactions and types of apparatus which are used in industry. They become familiar with the basic types of chemical reactions - combination, decomposition, displacement, double decomposition, oxidation and reduction etc.

They get acquainted with the same types of reaction when they study organic chemistry. However they meet a greater variety of each type of reaction and some new types of interaction in the organic chemistry field. Analysis of reactions used in the organic chemical chemistry shows that only about twenty are typical. However a detailed industry shows that only about twenty are typical. Only those study of all these reactions is impossible at school. Only those reactions which have a practical application should be studied more completely. The apparatus used in these processes should be typical of many branches of chemical industry. The following scheme indicates how some of these reactions can be introduced into school teaching.

Combination Reactions Hydrogenation is widely used in chemical industry. The essential ideas can be discussed in the topics 'Unsaturated hydrocarbons' and 'Aromatic hydrocarbons' when discussing with pupils the properties of ethylene, acetylene and benzene. However, hydrogenation of these hydrocarbons has very little industrial application at the present time and knowledge of the chemical nature of this reaction is only of theoretical significance. Pupils can be acquainted with the hydrogenation of olefines in catalytic cracking of petroleum in a discussion of the topic 'The natural sources of hydrocarbons'. Hydrogenation of aldehydes and unsaturated carboxylic acids can also be discussed under the appropriate headings, more complicated examples can be discussed when dealing with esters. Hydrogenation of oils for the production of solid fats is of great

Hydration Reactions Many important chemical reagents are obtained with the help of hydration reactions. The essential ideas are discussed in inorganic chemistry courses and the hydration of organic substances can be discussed in the topic 'Alcohols and phenols'. Hydration of ethylene should be taught in detail in of demonstrating the contact apparatus used in vapour phase hydration reactions.

Further examples of hydration can be discussed under the heading of 'Aldehydes'. Acetaldehyde is made by the hydration of acetylene and it is therefore desirable to study the chemical nature and the

Chlorination Reactions Chlorination is widely used in chemical industry. It can occur as combination with depending on the reaction conditions

Chlorination as the process of combination with chlorine can be discussed with pupils when dealing with 'Unsaturated hydrocarbons' and 'Aromatic hydrocarbons'. The syntheses of dichloroethane and hexachlorocyclohexane can be used as examples. The different conditions under which chlorination reactions occur should be mentioned. Dichloroethane is made by the chlorination at 20 - 30°C in the liquid phase in the presence of iron chloride as catalyst. Combination of chlorine with benzene goes at a temperature not higher than 40°C and chlorination in general.

Organic substances can also combine with hydrochloric acid and pupils should be acquainted with the reaction between ethylene and hydrochloric acid. The hydrochlorination of acetylene can then be discussed, to show how vinyl chloride is obtained in industry - activated charcoal catalyst saturated with mercuric chloride solution at a temperature of 120 - 180°C.

Alkylation reactions These are extremely important at the present time. High octane number additives and organic intermediates are obtained in this way. The main ideas can be discussed in the topic 'aromatic hydrocarbons' and it is possible to show that the alkylation of aromatic hydrocarbons by olefines creates side-chains and important intermediates such as ethyl benzene and isopropylbenzene.

$$\begin{array}{c} \text{CH}_2\text{-CH}_3 \\ \text{+ CH}_2 = \text{CH}_2 \longrightarrow \end{array} \begin{array}{c} \text{CH}_2\text{-CH}_3 \\ \text{+ CH}_3 \cdot \text{CH} = \text{CH}_2 \longrightarrow \end{array} \end{array}$$

This reaction is carried out at 85 - 90°C using an aluminium chloride catalyst. The use of alkylation reactions in increasing the chain length of saturated hydrocarbons can be treated in the topic 'Natural sources of hydrocarbons'. An example is the synthesis of iso-octane used as a fuel additive.

$$\operatorname{CH}_3 - \operatorname{CH}_3 + \operatorname{CH}_2 = \operatorname{C} \cdot \operatorname{CH}_3 \longrightarrow \operatorname{CH}_3 \cdot \operatorname{C} - \operatorname{CH}_2 - \operatorname{CH} - \operatorname{CH}_3$$

Polymerisation reactions Polymerisation of ethylene can be mentioned when dealing with 'Unsaturated hydrocarbons'.

The technical details of the process need not be discussed, but a comparison of the high and low pressure methods of preparation is desirable. The polymerisation of diene hydrocarbons is the basis of synthetic rubber manufacture. The basic synthetic rubber for normal use is the stereo-regular polyisoprene, although polydivinyl rubber may be important in future. The polymerisation of isoprene can be studied briefly, and the polymerisation of vinyl rubber in rather more detail. In this way students can be introduced to the idea of stereo-regular polymer structures and to the technology of polymer production.

Stereoregular polymerisation of divinyl takes place at a temperature of $30 - 50^{\circ}$ C in a special solvent using an organometallic catalyst (triethyl aluminium etc.).

The radical mechanism of polymerisation can be discussed under the heading 'Aromatic hydrocarbons' using styrene as an example. The polymerisation of formaldehyde should be dealt with in discussing 'Aldehydes' because this leads to the idea of hetero-chain polymers:

Preliminary ideas about co-polymerisation can be given in the topic 'Unsaturated hydrocarbons'. Once the properties of ethylene and propylene have been discussed their co-polymerisation according to the following scheme can be examined.

$$\begin{array}{c} \text{CH}_2 = \text{CH}_2 + \text{CH}_2 = \text{CH} + \cdots \longrightarrow -\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \cdots \\ \text{CH}_3 \end{array}$$
 This co-polymerisation process may be studied to familiarise the studied to

This co-polymerisation process may be studied in a more detailed way to familiarise the students with butadiene-styrene rubbers. The current technological details need not be studied but the conditions (temp. about Decomposition Reactions The Composition Reaction Reaction

Decomposition Reactions

The chemical nature and conditions for the dehydrogenation of n-butane and isopentane are of special importance as these reactions produce important intermediates in synthetic rubber chemistry. The conditions for the dehydrogenation of ethyl benzene can be mentioned when dealing with

$$CH_2 \cdot CH_3$$
 $\rightarrow CH = CH_2$
 $+ H_2$

This reaction occurs at about 600° C using zinc oxide with Cr $_2$ O $_3$, CaO and KOH as catalyst. A more detailed examination of dehydrogenation reactions can be made when discussing 'Natural sources of hydrocarbons' and to draw a parallel with the catalytic cracking of petroleum products.

The production of aromatic materials from raw materials rich in cycloparaffins may also be mentioned at the same time. In some conditions dehydrogenation is accompanied by ring closure - i.e. dehydrocyclisation. This reaction occurs during the reforming of petrol and it is also important for the preparation of aromatic hydrocarbons from saturated hydrocarbons. Dehydrogenation of ethanol can give either ethylene or ether according to the conditions, but this reaction has now almost lost its technical importance.

The decomposition of saturated hydrocarbons is fundamental to the cracking process and can be described when discussing the natural sources of hydrocarbons and catalytic cracking. The equipment used for 'boiling-layer' catalytic cracking can be described here.

Depolymerisation has no industrial significance but it is desirable to mention it when discussing polystyrene since pupils have not previously met an example of the preparation of homogeneous molecules by the decomposition of large molecules.

Displacement Reactions Chlorination of methane gives an opportunity discuss the chemistry and importance of

the conditions needed for the preparation of chlorosubstituted hydrocarbons. A temperature of 400 - 450 C is used. Substitutive chlorination of benzene requires a catalyst - iron or iron salts at an optimum temperature of 80 C. Technological details will include a description of a column-type reactor.

The industrial significance of nitration can be illustrated by using the nitration of methane, benzene and phenol as examples. The importance of nitration as an example of continuous operation in an industrial process can be stressed when discussing the nitration of benzene.

Double Decomposition Reactions Pupils will have learnt about esterification reactions when

dealing with carboxylic acids. The reaction is studied in more detail in the topic 'Fats and Esters'. It is desirable to explain both the chemistry and the conditions which are needed (liquid phase esterification requires sulphuric acid as a catalyst at a temperature sufficient for distillation of the ester, alcoholand water mixture; alcohol is used in excess in this reaction). The column type equipment for continuous esterification should then be described.

The esterification reaction is widely used in the synthetic fibre industry. This can be mentioned when discussing 'Carbohydrates' e.g. the preparation of di- and triacetyl cellulose as intermediates in the production of acetate fibres. Interaction between cellulose and nitric acid can be used as an example of esterification by mineral acids. The notion of hydrolysis as a converse reaction to esterification can be mentioned when dealing with 'Esters and Fats'.

Edible fats will be used less and less in future and the industrial hydrolysis of fats can be omitted. Hydrolysis of cellulose, however, can be discussed. A 0.1 - 4% solution of sulphuric acid is used as catalyst at a temperature of 150 - 170°C and at a pressure of 7 - 15 atmospheres.

Oxidation Reactions Pupils' attention should be drawn to the importance of conditions in the oxidation of methane. Formaldehyde is produced when oxidation is carried out at 450 - 500°C under 10 - 25 atmospheres pressure over a catalyst of copper and manganese compounds. Methanol is produced at a pressure of 100 -200 atmospheres. Oxidation of butane should be mentioned as an

example of an important new method for preparing acetic acid. The manufacture of fatty acids by the oxidation of parrafins is under rapid development, and the technological aspects should be

Isomerisation Reactions These reactions are important for showing involve a change in molecular weight. Isomerisation reactions can be students that reaction does not necessarily discussed when describibg catalytic cracking of hydrocarbons as, e.g., the formation of isobutane and isobutene from n-butane and n-butene. Vapour-phase isomerisation of n-butane goes at about 125 C under 12 - 18 atmospheres pressure using an aluminium chloride catalyst.

From all that has been written above it becomes clear that the school course in organic chemistry offers many opportunities for discussing reactions typical of industrial organic chemistry. At the end of the course some 5 - 6 periods should be devoted to summarizing the polytechnic aspects, and a problem class. the polytechnic aspects, and a problem class might be organised in which equations and reactions would be written for possible syntheses based on methane, ethane, butane, ethylene, acetylene and benzene. In this way pupils will become familiar with typical reactions in industrial

A course in industrial organic chemistry for first year arts sixth form

T. C. SWINFEN

Rugby School

The problem of the science topics which can profitably be studied by arts specialists is a perennial one. I have over the last few years developed the

course outlined below, and offer it as a contribution.

At Rugby, all boys not specializing in science follow, for a year after 'O' level, a general science course. This consists of three one-term courses, taking three periods and \(\frac{3}{4}\) hr homework weekly. Each term is complete in itself and unrelated to the others, for administrative reasons; they are not directed towards any external examination.

It seems to me that this kind of 'free' course can follow one of three broad

paths:

(a) To treat a narrow field in depth, in order to give knowledge of this field and (implicitly) an understanding of scientific ways. My physics colleagues have a course like this on atomic and nuclear physics.

(b) To teach scientific modes of thought explicitly by a course on various topics in, or aspects of, the history and philosophy of science. I tried this with a half-course on alchemy but with limited success: possibly an older or

more experienced class would have got more out of the work.

(c) To cover the applications of science in our present-day environment, by a descriptive account which of course runs the risk of being superficial. I feel strongly that science in schools should not only relate to 'real life' but also,

must (like justice?) be seen to do so. I follow this third path here.

The original idea came from Professor John Read's book, Through Alchemy to Chemistry, but my course, entitled 'Alchemy: Ancient and Modern' (modern alchemy seemed a good description of the production of textiles and plastics, etc., from somewhat unpromising materials like coal and oil), soon lost the Ancient section and expanded into its present form. This expansion, incidentally, took place long before I saw the A.S.E. Report on Science in Sixth-Form General Education.

Two additional points can be made:

(a) Most of the chemical products reaching the consumer are organic; the importance of sulphuric acid as a 'barometer of the country's prosperity', however great, is of little interest to the man-in-the-street; but what his shirt is made of may intrigue him.

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(b) The classes we have at Rugby range in attainment from those who have passed chemistry at 'O' level to those who have studied the subject for only two terms, and in ages from 15-plus to 17-plus. There is no uniformity of background or experience, so by entering a branch of chemistry hitherto

As I said above, there is risk that a course like this may become superficial. By using models of molecules, structural formulae and unbalanced equations where appropriate, and by continually stressing the relationship between molecular structure and the main properties of the substance being studied, I hope to avoid superficiality. (Molecular models of expanded polystyrene balls, as described in Education In Chemistry, January 1964, are useful because they are both large and to scale. I use the scale, I in to I Å.)

Over a quarter of the time is spent in the laboratory and, though I used to insist that the experiments were properly written-up, I now issue, a few days before the lab period, Gestetnered sheets of instructions carrying questions and 'boxes' for the answers. This liberates the homework time for more

Each boy at the end of the term writes an essay commenting on the course, so that I have the class's views on what they think I ought to develop or omit. The instructions for experiments, for example, have been approved and one

The search for a suitable textbook has met with little success so far. Next term I intend to give out sheets of notes, page references to library books, etc., rather than try to have a class text as such. Suitable reading can be found,

I have received valuable advice in correspondence and kind from Shell, Courtaulds, and ICI Dyes Division, as well as the pamphlets, films and

AN OUTLINE OF THE TERM'S COURSE

(Numbers in parentheses refer to the literature in Appendix A; letters to the Organic Chemistry

The usual introductory remarks about the differences between organic and The usual introductory remains about the unitables between organic and inorganic materials. Reminder about the meanings of atom, molecule, valency, formula. Discussion of structural formulae and the representation of them on paper. Isomerism treated in the same spirit as anagrams (1), (17),

Demonstrations: Typical organic compounds. Molecular models. Demonstrations. Typical organic compounds. Wiolecular models. The isomers of C₄H₁₀O, including the differing boiling points of n- and tertLaboratory: The fractional distillation of an alcohol/water mixture. I should like to use beer, ostentatiously methylated, but I expect it is illegal. The apparatus used is cheap and rugged (C); there appears to be some correlation between specialization in classics, and clumsiness, though this observation is probably only of value at staff parties!

OIL

Geology and theories of origin. Winning of oil from a well. Refinery processes, particularly primary distillation and cracking (thermal and catalytic) (2), (25), (36), (45).

Demonstrations: Shell wallcharts and booklet The Flow of Oil or (not so suitable because too simple) Oil for Everybody. Fractional distillation of crude oil (B). Cracking of paraffin wax or liquid paraffin to a volatile distillate (B). Specimens of distillation products.

Films: (Two periods, a week apart)

- 1. Prospecting for Petroleum Birth of an Oilfield
- 2. Refinery at Work (a bit too simple)
 Animal, Vegetable, Mineral

HYDROCARBONS

Paraffins and olefines mainly; acetylene and aromatics briefly. The idea of a homologous series and the trend expected in it. The differing reactivities of the hydrocarbon series (3), (12). Addition and substitution (46).

Demonstrations: Preparation of methane, ethylene, acetylene and the action on these of combustion, bromine water, and chlorine (B). Foretaste of the polymerization of unsaturated hydrocarbons.

Laboratory: Prepare an olefine on a small scale. Problems on this and the organic chemistry section (D).

PETROL

Formula, roughly, and place in the paraffin series. Production, with the economic necessity for cracking and reforming (4). Importance of the assorted by-products, such as ethylene and propylene. Flash Point. Four-stroke cycle and octane number.

Demonstrations: Shell wallcharts. Putting out a paraffin fire with paraffin (B). Model of a four-stroke engine. Cut-away Austin engine. January 1964 issue of Which?

Film: Octane Number.

SOAP AND DETERGENTS

Hydrolysis of fats and oils to soap. Nature and drawbacks (hard water) of soap. Explanation of cleansing action (5), (6), (18), (13), (21). Nullification of the effect of hard water by using suitable long-chain molecules which have soluble calcium salts. The other substances added to make up a typical washing powder—optical whiteners, blue colour, phosphates, etc.—and the action they have in improving the cleaning qualities or the advertising blurb of the washing powder.

Demonstrations: Unilever's wallcharts, filmstrips, and booklets Soap Through the Ages, Soap-Making and Soapless Detergents. Their recent publication, The Preparation of Soap, looks more suited to demonstration than for class use unless the students can give up some out-of-school time to do the experiment properly. The emulsifying action of soap and Teepol on mixtures of paraffin and water. The peptizing of mud. The wetting of fabrics.

Laboratory: Make crude soap and try out the demonstrations (E). 'Objective Washday Investigation' (F).

ESTERS

Compounds of acid and alcohol. Formation and hydrolysis. Fats and oils as the esters of long-chain acids with glycerol. Hardening of unsaturated oils to saturated fats by reduction with nickel and hydrogen. (Unilever are planning a school experiment on this.) Importance of this in the manufacture of margarine. (We have tested school margarine with dimethylglyoxime, but on the Government margarine universal at the time.) Possibility of the existence of a polyester such as terylene.

Demonstrations: Test-tube production of esters and, hence, possibility of using them as flavourings. Terylene specimens.

Laboratory: Prepare a pure specimen of ethyl acetate, by the conventional route. Repeat the test-tube preparation of esters, choosing hitherto unfamiliar combinations of acid and alcohol.

PLASTICS AND POLYMERS

THERMOPLASTICS

Meaning of thermoplastic, polymer, monomer, polymerization. The plastics based on the polymerization of CCC (7, 14, 19, 22, 29, 32, 34, 37, 38, 40, 41, 42, 43, 47, 48, 49, 50, 51, 52, 53, 54), i.e. polythene (39), polypropylene, polystyrene, and their paraffinic behaviour; also polytetrafluoroethylene,

polyvinylchloride, polyacrylonitrile, polyvinylacetate, polymethyl-α-methylacrylate. Polyesters as linear polymers formed by condensation reactions: terylene and glyptal (8).

Demonstrations: Paul Jennings' 'Propylegomenon' and its counterblast 'Polythalamion' from the Observer. Specimens and molecular models galore. Preparation of polystyrene, and of a glyptal resin. By using excess glycerol. one can, with luck, stop at the linear polymer stage, and cross-link the molecules later.

Laboratory: Make polystyrene, poly(p-hydroxyethoxybenzoic acid) (B).

THERMOSETTING MATERIALS

The idea of cross-linking linear polymer molecules to give a rigid threedimensional molecule. Use of an inert filler, e.g. in fibreglass or laminated plastics (15).

Demonstrations: Models. Finish the glyptal resin. Weetabix 'Puffkins' (B). Bakelite (9), (55), (56), (57).

Laboratory: Glyptal. Urea/formaldehyde (B), (26).

TEXTILES

Cellulose, both as a natural material (cotton) and regenerated (10, 16, 23, 30, 35, 54). Viscose rayon and its structure. The esterification of the exposed hydroxyl groups to cellulose acetate, and the effect this has on the properties of the material, e.g. absorption of water. Polyesters, already covered; polyamides like wool and nylon.

Demonstrations: Specimens of products and intermediates. Courtauld's flow diagrams. Cellulose xanthate made from filter paper or cotton wool (58). The 'Nylon Rope Trick' (50).

Laboratory: Cuprammonium viscose. I supply freshly precipitated copper hydroxide, to start everyone off quickly. The school doctor let us have several hundred hypodermic syringes, of the 'use once and discard' type: these come in very handy for a variety of uses (chromatography and Victor Meyer, as well as the one here).

Film: Point of New Departure (survey of fibres and the discovery of Terylene).

DYES

I don't bother with the details of what the molecule of the dye looks like or I don t bother is coloured; it is enough that dyes can be acidic, basic, the inwhy the dye as soluble substances, etc. Vat, direct, mordant, soluble product of reacting two soluble substances, etc. and azo dyeing-pointing out also the remarkable specificity of the dye to a particular fabric (11), (20), (24), (28), (33).

Demonstrations and Laboratory work chosen from: Picric acid, which dyes wool directly (yellow) but not cotton. Methylene blue, which is less successful as a direct dye on cotton than when the cotton is first soaked in a solution of potassium antimony tartrate, squeezed dry, then dipped in tannic acid solution and squeezed dry, before dyeing. Fast green and mordant (59). Cotton dipped in nickel sulphate, then in alkali, then in dimethylglyoxime solution. Cotton similarly impregnated with alumium hydroxide, dyed with alizarin. Cotton, spotted with alkaline beta-naphthol and dried, then developed with a solution of phenyl-diazonium chloride. ICI Three-Colour Dyebath. Skeins of viscose rayon, acetate rayon and silk are dyed in a blue dyebath containing, in fact, three dyes and come out blue, yellow, and maroon respectively.

In a 13-week term, this brings me up to the school exams. In a shorter term, something must be left out, and this is obviously a matter for personal preference.

Appendix A-Suggestions for Reading

Some of these references are too difficult for the students to follow up. I have not yet read Men and Molecules by Theiler (Harrap) which has been recommended to me, and there must be many similar gaps.

F. W. Gibbs, Organic Chemistry Today (Penguin)

(1) pp. 1-5, 9-13 (2) pp. 25-36 (3) pp. 13-16 (4) pp. 36-40 (5) p. 78 (6) pp. 135-40 (7) pp. 44-7 (8) pp. 85-8 (9) pp. 56-8 (10) pp. 153, 156-8,

K. Hutton, Chemistry, Man's Conquest of Materials (Penguin)

(12) p. 61 (13) pp. 188-9 (14) pp. 140-4 (15) pp. 144-6 (16) pp. 129-39. CIBA Ltd., The Story of Chemical Industry in Basle (CIBA)

(17) pp. 224-30 (18) pp. 213-23 (19) pp. 201-9 (20) pp. 86-9, 118-53. S. A. Gregory, Chemicals and People (Mills and Boon)

(21) Ch. 6 (22) Ch. 11 (23) pp. 103-6 (24) Ch. 8.

W. Haynes, This Chemical Age (Secker and Warburg)

(25) Ch. 13 (26) Ch. 19 (27) Chs. 16, 17 (28) Chs. 3, 4.

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(37) Journal, Sept. 1961, pp. 323-30

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Index of Chemistry Films is very useful.

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New Scientist
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(42) 22 June, 1961, p. 706	(43) 23 Jan., 1964, p. 224

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(55) p. 1022. H. N. Alyea, "Tested Demonstrations in Chemistry", Journal of Chemical Education, (56) section 22–18 (57) 22–48s et seq. (58) 22–66s and 22–67s (59) 22–41s.

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Shell International Petroleum Co., Petroleum Handbook and many other publications.

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A. Allcott, Plastics Today (Oxford).

Appendix B-Details of some experiments

OIL

Fractional distillation of crude oil (Shell)

Shell suggest mixing 10% gasoline, 20% kerosene, 20% gas oil, 20% light lubricating oil and 30% fuel oil to make a suitable 'crude' oil. I have some genuine crude oil and have not yet had to mix an artificial one. Distil, in quickfit apparatus, the later fractions under vacuum. I have not found any need for a long fractionating column. Shell suggest a preliminary distillation to find the temperature range of the fractions taken, before the class demonstration.

Catalytic cracking of paraffin wax (Shell)

Dry the catalyst (Fuller's Earth, Surrey Finest Grade) in a flask over a Bunsen for 15 minutes, then pour it into molten wax in a distilling-flask fitted with a water-condenser. Mix and heat the flask hard. A volatile distillate, containing unsaturated hydrocarbons, collects. The yield is small and slow. The value of this experiment lies in the production of a liquid from a solid hydrocarbon, manifestly the degradation of large molecules. The liquid can be shown to be unsaturated by adding a drop of bromine in carbon tetrachloride, and can be made into a detergent by the action of about half its volume of fuming sulphuric acid, added dropwise, slowly. This mixture, after neutralization with alkali and some purification, has the characteristics of a weak solution of a detergent.

Catalytic cracking of paraffin oil (J. Chem. Ed. and Science Masters' Book, Series 3, p. 95)

Fit a test-tube with a delivery tube, having put in 5 ml of paraffin oil and a lump of steel wool ($\mathcal{F}.C.E.$), or oil-soaked asbestos and pieces of pot (S.M.B.). Heat the solid hard, and boil the oil so that the vapour passes over the hot solid. The product can be shown to be unsaturated.

The reaction between chlorine and acetylene

Put about one in depth of bleaching powder in a boiling-tube held vertically in a clamp. Cover with dilute hydrochloric acid, then add a small piece of calcium carbide. The spontaneous reaction shoots orange flame and carbon smoke rings at intervals for some time.

Putting out a paraffin fire with paraffin (Shell)

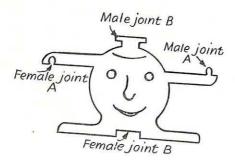
Support a medium-size baking tin to slope slightly over an unlit Bunsen. Have a 1-litre beaker (and a CO₂ fire extinguisher) handy. Fill the beaker with paraffin, also put some in the tin. Drop lighted matches into the tin and show that there is no resultant fire (temperature below flash point). Heat the shallow end of the paraffin until it does catch fire when matches are dropped in, then put out the Bunsen. When the blaze looks spectacular, pour the contents of the beaker into the tin smoothly and quickly. When the temperature of the paraffin drops below its flash point, the flames go out. Don't let the paraffin in the tin get too hot.

Preparation of poly-hydroxyethoxybenzoic acid (Courtaulds)

Heat a few gm of the monomer in a test-tube over a small flame. When the solid has melted (180°) insert a 360° thermometer and raise the temperature to about 280°, then gradually to 330° while the reaction takes place with evolution of water vapour. The melt gradually becomes more viscous. Samples can be spotted on to a cold surface and the final product is a transparent, glass-like solid. At a suitable point in the cooling, fibres can be pulled from the viscous melt.

$$n \text{HO.CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{COOH} \rightarrow -\left[\text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO.O}\right]_n^n + n \text{H}_2 \text{O}$$

Weetabix 'Puffkins' (plastic figures given in packets of 'Puffkins', a now obsolete breakfast cereal)



These little figures come in several colours and can be joined together horizontally and vertically.

Condensation of urea and formaldehyde

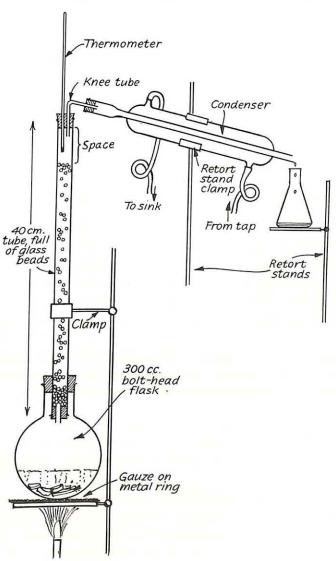
Shake strong formalin with urea in a test-tube until the solution is saturated. Add one drop of concentrated sulphuric acid and a white solid 'grows' along the tube.

Name:

Appendix C-Experiment sheet

DISTILLATION OF IMPURE ALCOHOL

Work in pairs. Put about 100 cc of impure alcohol and a few pieces of broken



pot in the round-bottomed flask provided. Fill the long glass tube with glass beads. Steady the flask and tube with a couple of clamps (and a ring and gauze under the flask) taking care to protect all glass from contact with metal by using scrap paper. Insert the cork, thermometer and knee-tube. Steady the condenser in another clamp on a second stand, and cautiously mate the two pieces of apparatus. Connect up the rubber tubing as in the diagram and start a flow of water. Begin heating the contents of the flask; when these boil, simmer the brew gently so that the vapour rises up through the beads and flows into the condenser fairly slowly. When the thermometer reads about 78°C collect the distillate. Don't collect any liquid coming over while the thermometer reads from 85-95°. Keep it, again, from 95-100°. Record the names of the two liquids you collect, the temperatures at which the bulk of the fraction came over, and the reason why you rejected the fraction of range 85-95°.

1	Temb
2	Temp. 1
Reason:	

- (a) Bits of pot cause the boiling to be smoother and less likely to 'bump' or
- (b) Alcohol vapour condenses at a lower temperature than water vapour. A mixture of both leaves the boiling liquid, but the glass beads, when the experiment is running smoothly, cool the water vapour to water while not being cold enough to condense alcohol. Condensed liquid trickles down the condenser. This meets upcoming vapour and tends to condense water out of it while the hot vapour evaporates alcohol out of the downcoming

If the liquid flow is too great, this action is swamped. Collecting distillate in fractions, each with its own characteristic boiling point, is called 'fractionation' and the glass beads fill, here, a 'fractionating column'. There

These sheets are in manuscript rather than typed, I think this makes them

The fractionating column is about $1\frac{1}{2}$ cm diameter, and the beads are kept in by a cork at the bottom carrying a centimetre of glass tubing just narrower than the beads, though I don't think this last dimension is critical.

I collect these sheets at the end of the lesson and can check them quickly to

find out how well the work has been understood and how far the boys have managed to get.

Appendix D-Experiment sheet



(1)
$$CH_3$$

Tertiary-butyl alcohol CH_3 — C — OH
 CH_3

is at room temperature a solid, and normal-butyl alcohol,

a liquid. Which would you expect to have the higher boiling point, and why?

Now find out, by heating each in a test-tube gently until it boils and holding a thermometer in the mouth of the tube. AVOID HAVING A FIRE—don't let the vapour catch the flame of the Bunsen. Give the *steady* reading on the thermometer.

an vou	explain	this in t	erms of mole	cular stru	cture?	
an you	ехриин	i this the t	erms of more	cuiar siru	ciures	

(2) n.b. BROMINE IS DANGEROUS

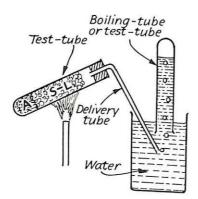
Find out which, of the pair, styrene and phenol, is saturated, and which is unsaturated, by dissolving about 1 cc or 2 gm of each in turn in a few cc of carbon tetrachloride (solvent) and adding 2 cc of the given solution of bromine in the same solvent.

Phenol and bromine are both dangerous. Keep them well away from faces and skin, but if you fail to do this first WASH with lots of water, THEN TELL ME.

Write down what you see happen.

Phenol	sat./unsat.
Styrene	sat./unsat.

(3) Prepare propylene and collect it over water in a boiling-tube as in the diagram. Find out whether it is flammable or not and, using bromine-water, whether it is unsaturated. Write the equation for its preparation.



A is asbestos soaked in propyl bromide CH3. CH2. CH2Br.

S-L is soda-lime (which behaves as if its formula were NaOH). Don't pack

it in too tightly.

Heat the soda-lime and flip the flame at the asbestos so that a little of the (volatile) propyl bromide vapour passes over the soda-lime and its molecules are cracked to those of propylene. The asbestos must therefore not be heated except on purpose. Drive the air out of the tube before trying to collect any

Equation:

Appendix E-Experiment sheet

SOAP

Name:

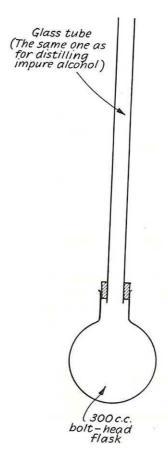
(1) Put into the bolt-head flask about a teaspoonful of olive oil or lard, one teaspoonful of sodium hydroxide pellets (which are dangerous to the skin), one test-tubeful of ethyl-alcohol, and 100 cc of bench sodium hydroxide solution.

Don't take too much fat or you will never finish making the soap. Connect up the glass tube as shown, and steady the apparatus in the usual

stand.

Bring the contents to the boil and then let them simmer slowly for about half an hour. Try not to let anything squirt from the top. Leave the apparatus, with your name on it, on the side bench until next time.

Reheat the liquid and pour it hot into a 400-cc beaker about half full of brine. Stir vigorously. The scum is crude soap. This can be filtered off



under suction, rinsed with water, squeezed in a cake, and used for washing with. It is still full of sodium hydroxide so will be harmful for delicate skin. It can be improved by adding to it a little water, bringing to the boil, then stirring for a few minutes followed by adding hot brine slowly until the mixture doesn't stick to the stirrer. Cool overnight and keep the solid layer.

Describe the	colours and ev	ents here:	

Observations	_ 7	0
Observations	and	Comment

Meanwhile when opportunity occurs: (2) Shake a few drops of paraffin in half a test-tube of water. Repeat with soap or detergent solution.

(2) (3)

- (3) Boil some mud with half a beaker of water for a minute or two. Filter and comment on the filtrate. Repeat with soap or detergent solution.
- (4) Drop a piece of cotton-wool into a gas-jar of water and time how long it takes to sink.

Repeat with soap or detergent solution and a piece of cotton-wool, as like the first as possible.

Note:

In (1) a reflux water condenser would be better than an air condenser, but this is cheaper. Unilever have an experiment which is better than (1), but it would, I think, take four periods to complete this sheet instead of two.

(4)

Appendix F—Experiment sheet

AN OBJECTIVE COMPARISON OF WASHING POWDERS

Name:		
vame:		

This is actually rather unfair. Write at the bottom the protests which might be made by the manufacturer, when you have finished.

Half fill a large waterbath with hot water and set it over a Bunsen (no gauze needed) to boil.

Meanwhile dirty a white handerchief with the dirt and the colour provided.

When the water is boiling, put in two tablespoonsful of one of the washing powders provided, add the handkerchief and slosh the handkerchief around for exactly one minute; then put out the Bunsen and continue stirring the mixture with a glass rod until 10 minutes altogether have elapsed.

Pour off the water, half fill the bath with cold water, slosh for a quarter of a minute, pour out the water. Refill and repeat.

Squeeze out the handkerchief. Decide how satisfied you are with the cleanliness of your handkerchief (a) in the middle of the lab, (b) near a window. Hold the handkerchief in the light from an ultraviolet lamp. (Remember not to look at the lamp yourself.)

Compare your handkerchief with the other clean (?) ones produced by your colleagues.

Powder no.	Cleanliness: lab	
u u	,, window	
	Under u/v light	
	Better powders were	
	Worse ,, ,,	
	This powder was actually	1 21
	The comparison is unfair because	
	7	

Notes:

(1) I used mud/olive oil and methylene blue last time, but it defeated most of the powders.

(2) One has to leave the packets around for the class to make their protest: otherwise they won't know which detergents are for delicate woollens and which not.



7. Selected topics

7. Sujets divers

This section contains articles on a number of unrelated topics which do not conveniently fit into the main sections 1-6 of this volume.

RADIOCHEMISTRY

The article on radio-activity is based on a talk given to high school students at Expo 67. The author describes a large number of demonstrations that can be used to illustrate many of the important phenomena of radio-activity. He outlines the relevant theory and discusses possible applications of radioactive substances.

J. Golden and A. G. Maddock discuss a radio-active half-life experiment suitable for college courses. An experiment intended for class use requires cheap and relatively innocuous materials, a short half-life and radiation that is easily detectable on fairly simple and robust equipment. A solvent extraction method is used in which Pa nuclides are extracted from an aqueous uranyl salt solution into a ketonic solvent. The decay of ^{234m}Pa is then followed.

GEOCHEMISTRY

This topic is not often discussed in school courses, but it is one of great general interest. Many topics in general, inorganic and physical chemistry can often be exemplified by material of geochemical significance. The article by L. G. Sillén shows how the phase rule can be applied to a discussion of the composition of sea water and the atmosphere. He includes some useful tables giving details of concentrations of substances found in sea water.

CO-ORDINATION CHEMISTRY

Much of the rapid development in inorganic chemistry in recent years has been concerned with the preparation and reactions of co-ordination compounds. Dr. G. G. Schlessinger's La présente section comprend des articles relatifs à divers sujets qui n'ont pu trouver place dans les sections de ce volume numérotées de 1 à 6.

RADIOCHIMIE

L'article sur la radioactivité est fondé sur une causerie donnée à l'« Expo 67 » qui s'adressait à des élèves de l'enseignement secondaire. L'auteur décrit de nombreuses démonstrations qui peuvent servir à illustrer un grand nombre des importants phénomènes de radioactivité. Après avoir donné un aperçu théorique de la question, il examine diverses applications possibles des substances radioactives.

J. Golden et A. G. Maddock décrivent une expérience portant sur la période radioactive qui convient à l'enseignement supérieur. Une expérience destinée à l'enseignement doit utiliser des substances peu coûteuses et relativement inoffensives, ayant une courte période et dont le rayonnement soit facilement détectable à l'aide d'appareils assez simples et robustes. On utilise une méthode d'extraction par solvant, dans laquelle des nucléides de Pa sont extraits d'une solution aqueuse de sel d'urane et passent dans un solvant cétonique. On observe ensuite la désintégration de ^{234m}Pa.

GÉOCHIMIE

Cette matière figure rarement dans les programmes scolaires, bien qu'elle présente un grand intérêt général. De nombreux sujets de chimie générale, minérale et physique peuvent être illustrés par des exemples qui se rattachent à la géochimie. Dans son article, L. G. Sillén montre comment on peut appliquer la règle des phases à une étude de la composition de l'eau de mer et de l'atmosphère. L'article comprend quelques tableaux fournissant des détails utiles sur la concentration des substances qui se trouvent dans l'eau de mer.

CHIMIE DE COORDINATION

Les progrès rapides enregistrés ces dernières années dans le domaine de la chimie minérale ont trait dans bien des cas à la préparation et aux réactions des composés de coordination. "short course" on co-ordination chemistry deals first of all with the theories of bonding between a metal atom and its ligands in these compounds. He then surveys the different types of isomerism displayed by co-ordination compounds and finally discusses applications—in, for example, the extraction of metals, catalysis, industrial chelating agents and metal complexes of biological significance such as haemoglobin.

Le « cours rapide » du Dr G. G. Schlessinger sur la chimie de coordination traite tout d'abord de la théorie des liaisons entre un atome métallique et ses ligands dans ces composés. Il étudie ensuite les divers types d'isomérie présentés par les composés de coordination et, pour finir, examine diverses applications, concernant par exemple l'extraction des métaux, la catalyse, les agents chélateurs industriels et les complexes métalliques ayant une importance biologique, comme l'hémoglobine.

RADIOACTIVITY— The plight of unhappy nuclei

J. M. ROBSON, Physics Department, University of Ottawa, Ottawa, Ontario.

Detection of Radiation

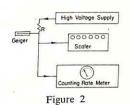
In order to study radioactivity we use some device sensitive to radiation, called a detector; a very simple type is the 'Geiger Counter'. It consists basically of a tube containing a gas at reduced pressure, usually about onesixth of that of the atmosphere. A thin wire down the centre of the tube is held at a positive voltage relative to the wall of the tube; this voltage is kept just below the value at which the tube would break into a continuous discharge like a 'neon' tube. Whenever an energetic charged particle passes through this tube it will provoke a temporary discharge which will lower the voltage on the central wire. A special mixture of gas is used in the tube which has the ability to 'quench' or stop in discharge soon after the particle has passed through. Thus the voltage only decreases momentarily and a pulse appears on the wire to indicate the passage of the particle. Figure 1 shows the essential structure of an end window Geiger tube which, as its name suggests, contains a thin window at one end to permit particles which are not too penetrating, such as low energy electrons, to enter the tube and be detected. Many other types of Geiger tubes are available but all basically work in the simple manner indicated above.

The pulses which appear on the central wire can be counted by an electronic device called a 'scaler'. This will indicate the arrival of a pulse by a change in its indicator lights and can

Figure 1
A simple end window Geiger counter.

be used to count the number of pulses arriving in a given time. It also, of course, generally indicates the rate at which the pulses are arriving by the rate at which its indicator lights change. This rate of arrival of the pulses, or 'counting rate', can also be measured quantitatively by a different type of electronic circuit called a 'counting rate meter'. This measures the number of pulses arriving per second and indicates this rate on a meter scale. Thus a useful arrangement is to connect both a scaler and a rate meter to the output of the Geiger as indicated in Figure 2.

If we connect up such a system we find that, even with nothing near the Geiger, the counting rate is not zero; there is always a steady background rate due to radiation coming from



A Geiger counter connected to a scaler and a counting-rate-meter. The high voltage supply and the resistance R are often incorporated in the same box as the scaler.

outer space. This radiation is usually called 'cosmic radiation' and persists even with quite extensive shielding around the detector. (In the small detectors used for illustrating this talk it amounted to about 30 counts per minute).

Demonstration of Radioactivity

If a piece of ordinary cobalt is placed near this detector nothing in particular happens; the counting rate will remain at about the background level. If however a similar piece of cobalt which has been irradiated in a nuclear reactor is placed near the detector the counting rate rises spectacularly and remains high as long as it is nearby. The two pieces of cobalt look the same but obviously the second is emitting something which affects the detector, while the first is apparently not.

Furthermore if a piece of normal bismuth is placed near the end window of the detector nothing unusual happens whereas with a similar piece of bismuth extracted from uranium ore the counting rate will increase considerably. Both the cobalt which had been irradiated and the bismuth extracted from the uranium ore are said to be 'radioactive' whereas the ordinary cobalt and the ordinary bismuth are stable or 'non radioactive'.

There is, however, a difference between the cobalt and the bismuth which can easily be demonstrated with the help of our Geiger counter. Suppose we place the bismuth near the detector and try putting some thin pieces of aluminium foil between them. Even with a very thin piece of aluminum the counting rate is reduced and with a piece 1/16 inch thick the rate is practically down to the background

4

Thin mico window Gas at a pressure of a few cm of mercury

R (1000 volts)

Incoming Metal tube charged on central wire

Based on a talk to a group of high school students at Expo 67. April 29. The talk was illustrated by a sequence of live demonstrations which are, of necessity, only rather briefly described in the article.

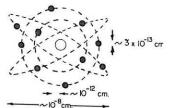
level without the 'source' present. However, repeating this experiment with the radioactive cobalt gives a very different result. The 1/16 inch of aluminum has practically no effect at all and the counting rate is almost the same with or without it in place. It takes about 1/4 inch of lead to have a noticeable effect and at least an inch of lead to reduce the counting rate to anything approaching the background

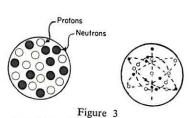
This type of experiment leads to only one type of conclusion: the radiations emitted from the two sources are very different. That from the bismuth is easily stopped while that from the cobalt in its little container is very much more penetrating.

Atomic Structure

To understand this difference we must consider the structure of atoms. An atom consists of a relatively heavy central nucleus surrounded by a cloud of electrons. Nuclei are positively charged and in a neutral atom the negative charge of the electrons exactly neutralizes this positive charge. The number of electrons in a neutral atom, or alternatively the positive charge on the nucleus, identifies the chemical element and is usually indicated by the symbol Z, the atomic number. Z = 1 is hydrogen; Z = 2 is helium and so on with the last naturally-occurring element, uranium, hav-Z = 92. Figure 3 depicts in a very schematic way the structure of an atom of neon for which Z = 10.

In this sketch the black dots represent electrons and are depicted as moving in nicely defined orbits. This is an oversimplification but is reasonable for our purposes. The central circle is the positively charged nucleus and its structure is suggested in the lower left sketch of Figure 3. There are two types of particles inside it - neutrons and protons. The neutrons are electrically neutral whereas the protons are positively charged, each carrying the same charge as an electron but of opposite sign. Again the sketch is idealized but it correctly indicates one basic difference between nuclei and atoms: the former are very dense objects with the nucleons (either neutrons or protons) being closely packed, whereas the atom is a very open structure with the electrons relatively far apart. The nucleons are, of course, not stationary and their motion is quite complicated. It is sketched in a simplified way in the lower right hand sketch where the neutrons and protons are shown in orbits, rather similar to those of the electrons in the atom. Obviously there are differences and one should not take





Simplified schematic of the structure of an atom of Ne20. The top sketch represents the whole atom while the lower two indicate an isolated nucleus.

these sketches too seriously; they do however give a reasonable general idea of what is happening inside atoms.

The particular nucleus in Figure 3 contains 10 protons and 10 neutrons or a total of 20 nucleons. This would be described by the following symbol,

10 Ne20

in which the 10 indicates the number of protons or value of Z and the 20 indicates the total number of nucleons, usually indicated by A, the mass number. The element neon always has Z = 10; there may be different values of A, however, and in natural neon about 91% of the atoms have nuclei with A = 20 while about 9% have A = 22. These different types of nuclei therefore have the same Z but different numbers

of neutrons. They are said to be two

Radioactive Nuclei

different 'isotopes' of neon.

Now let us consider cobalt. Normal naturally-occurring cobalt contains 27Coso. Each nucleus therefore consists of 27 protons and 32 neutrons. These nuclei are quite stable and happy and will stay unchanged indefinitely provided they are left alone. However, if a piece is placed in a nuclear reactor it finds itself in the presence of a large number of neutrons produced by the fission chain reaction in the reactor. Many of the 27Co50 nuclei will capture a neutron becoming 27Co60. This new isotope has 27 protons and 33 neutrons and the out-of-balance between the number of neutrons and protons has increased. The nuclei would prefer

to have a more balanced ratio between these numbers, such as 28 protons and 32 neutrons. A slight excess of neutrons is needed so that the nuclear force can overcome the cumulative electrostatic repulsion between all the positively charged protons.

In order to make this change a neutron inside the 27Co60 must change into a proton. This is not an easy change and it may take quite a long time before an individual ${}_{27}\text{Co}^{60}$ nucleus changes into a ${}_{28}\text{Ni}^{60}$ nucleus. The average time depends on detailed energy considerations but is always long compared to the time scale of other nuclear changes — in this case the time for half of the 27Co60 nuclei in a given sample to change into 28Ni00 nuclei, or the so called 'half life', is about five years. Though Co60 is unhappy it still takes it a long time to cure its ills!

The cure, when it comes, is quite sudden! Co60 emits an electron and an almost unobservable particle called an antineutrino. This latter particle is emitted in order to conserve various quantities which are unchangeable in physics: energy, angular momentum and a thing called lepton number. Since it is almost unobservable I won't consider it in detail here. The electron is, however, very observable and in the case of the radioactive bismuth source it was these electrons which were detected by our Geiger counter. If the cobalt source had not been in a glass bottle we would also have detected the electrons emitted in its radioactive decay. The electrons were absorbed by the glass and the radiation we were then detecting was due to gamma rays which followed the upheaval inside the nucleus. We will discuss them further in a moment. The process is indicated by the following formulae:

$$\frac{27^{\text{Co}^{59}} + \text{n} \rightarrow 27^{\text{Co}^{60}}}{27\text{p} + 32\text{n}} \quad (1)$$

$$\frac{27^{\text{Co}^{60}} \rightarrow 28^{\text{Ni}^{60}*} + \text{e}^{-} + \text{v}^{-}}{28\text{p} + 32\text{n}}$$

Equation 1 indicates the capture of a neutron by a nucleus of Co59 to form a nucleus of Co60, and equation 2 shows the subsequent radioactive decay of the Co60 nucleus. The star associated with the Ni⁶⁰ indicates that it is created in an 'excited' state rather than in the normal 'ground' or unexcited state of Ni60 nuclei found in nature. It is the transition of the Ni60* nuclei to Ni60 nuclei which causes the emission of the penetrating radiation, called gamma radiation. The symbols e- and v indicate the electron and the antineutrino emitted in the radioactive decay of a Co60

JANUARY, 1968

In the case of our source of Bi²¹⁰ the equation is written as follows:

$$_{83}Bi^{210} \rightarrow _{84}Po^{210} + e^- + v^-$$

In this case the Po²¹⁰ is formed in its ground state and no gamma rays follow the transition. The only indication of the radioactive decay is the emission of the electron. The absence of gamma rays accounts for the easy way in which we were able to shield the detector from the Bi²¹⁰ source. Their emission from Ni⁶⁰⁸, however, is the reason why a considerable thickness of lead is required to stop the Geiger from detecting the Co⁶⁰ source.

Emission of Gamma Rays

Let us now consider in more detail the events that follow the decay of Co60 into the excited state of Ni60. They are depicted in Figure 4 which tries to schematically show a nucleus of Co60 in the top left circle going through intermediate stages to its final state as a stable unexcited nucleus of Ni60, shown in the lower right circle. In the top left circle 27p + 32n represents 27 protons and 32 neutrons inside a Co60 nucleus. The 33rd neutron is for simplicity shown in a circular orbit. The radioactive transition which will perhaps not occur for many years after the formulation of the Co60 is shown by the change from the top left circle to the top right circle. The neutron has changed into a proton and is in the same circular orbit. The electron and antineutrino are shown leaving the newly formed Ni^{60*} nucleus. This 28th proton, however, finds itself in an orbit which, though appropriate for the 33rd neutron, is at a higher energy than is necessary and it proceeds to jump down to a lower energy orbit. For detailed reason it does this in two jumps losing 1.17 MeV in the first and 1.33 MeV in the second. The jumps provoke the emission of gamma rays which are uncharged wave packets often known as photons. Thus in the first jump a 1.17 MeV gamma ray comes out while in the second the gamma ray has an energy of 1.33 MeV. The symbol MeV stands for million electron volts and is a unit of energy - one MeV is the kinetic energy acquired by an electron after being accelerated through a potential difference of one million volts. 1 MeV is equivalent to 1.6 x 10-13 joules and is therefore by everyday standards only a very small amount of energy. On the atomic scale, however, it is large - the photons of visible light have an energy of only 3 eV and the X rays used in radiology about 40,000 eV.

These gamma rays come out very quickly, as indicated in Figure 4. Since

+ 27 p + 32 n + 32 n + 27 p + 32 n 1.33 MeV 1.427 p 1.437 p 1.437 p

Figure 4
Radioactive decay of Co⁶⁰ and the subsequent gamma ray emission from Ni⁶⁰*.

they carry no electrical charge they do not react strongly with matter and can readily pass through thin sheets of aluminum as noted in our experiment with the Geiger counter. They do, however, occasionally interact with atoms and in such interactions they knock out electrons. It is such interactions with the walls of the Geiger counter which enabled it to detect the gamma rays the discharge was actually caused by these electrons and not by the gamma rays themselves. Since the probability of such an interaction is low the Geiger counter is quite an inefficient detector of gamma radiation and only detects about 2 percent of the gammas incident upon it. We will discuss a more efficient



Figure 5

Pu-Be neutron source. The Pu-Be alloy is at the centre and is surrounded by paraffin wax.

detector shortly. First however I wish to demonstrate the creation of a radioactive source by neutron addition to stable nuclei.

Activation by Neutron Capture

This would normally be done by putting the sample in a nuclear reactor where there are tremendous numbers of neutrons diffusing around. For demonstration purposes, I have made a portable neutron source which, though very weak by comparison with a reactor, produces a sufficient number of nutrons to activate some samples.

The source is shown in Figure 5 and consists of a small piece of plutoniumberyllium alloy at the centre surrounded by paraffin wax. Plutonium does not occur naturally but can be made in a nuclear reactor. It has many interesting properties and the useful one in this device is that it is alpha radioactive. The radioactivity described above is beta radioactivity in that a beta particle - the same thing as an electron - is emitted in the decay. In alpha radioactivity an alpha particle, or nucleus of helium, is emitted and in the particular case of plutonium the decay can be represented by

$$94Pu^{239} \rightarrow 92U^{235} + 2He^4$$

 $_2$ He⁴ is usually indicated by α , the symbol for an alpha particle. The half life of Pu²³⁹ is about 25,000 years and consequently, though the source we have is gradually losing its strength, this loss is negligibly slow on our time scale. The particular piece we are using emits about 7 x $^{10^{10}}$ alpha particles per second showing that there are about 7 x $^{10^{22}}$ nuclei of Pu²³⁹ present!

The plutonium is mixed with beryllium in the alloy used in this source so that the alpha particles can strike beryllium nuclei. Most of them however lose their energy by interactions with the electrons in the atoms of the plutonium or the beryllium but about 1 in 10,000 cause the following nuclear reaction to occur with a beryllium nucleus:

$$_4\text{Be}^9 + _2\text{He}^4 \rightarrow _6\text{C}^{12} + \text{n}$$

These neutrons are produced with energies of the order of a few MeV and are going too fast to easily induce radioactivity in other stable nuclei. They can be slowed down by successive collisions with hydrogen nuclei or protons. Thus in our neutron source paraffin is put round the PuBe alloy in order to slow down the neutrons until they come into thermal equilibrium with the hydrogen in the paraffin molecules; they are then known as 'thermal neutrons'. This process is depicted in Figure 6 and is occurring all the time in our neutron source. The number of

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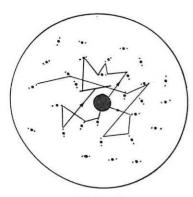


Figure 6
The slowing down of neutrons by the paraffin surrounding the Pu-Be in the neutron source.

neutrons crossing an area of 1 sq. cm. in the paraffin is about 10⁴ every second due to this scattering process. To activate a sample we must put it in this 'flux' of neutrons; in our neutron source a hole fitted with a polythene plug enables us to place a small sample in an appropriate region. The hydrogen in the polythene is just as good a scatterer as the hydrogen in paraffin so the neutron flux is not reduced by this simple 'sample irradiation facility'.

It would take too long to irradiate a piece of cobalt to a suitable activity and therefore, we are using a piece of silver as an alternative. It is not now radioactive as can be seen by putting it in front of our Geiger counter - there is no change in the low background counting rate. To irradiate it we put it in the slot in the polythene rod and insert the rod in our neutron source. After an irradiation of about a minute we withdraw the rod and put the silver foil in front of the Geiger and note that it counts at a very high rate. The counting rate decreases fairly rapidly at first and then more slowly, eventually being quite low. This behaviour is easy to understand when we take into account the fact that normal silver consists of a mixture of Ag109 and Ag110 atoms. The nuclear reactions occurring during the activation are as follows:

$$_{47}Ag^{107} + n \rightarrow _{47}Ag^{108}$$

 $_{47}Ag^{109} + n \rightarrow _{47}Ag^{110}$

The Ag¹⁰⁸ and Ag¹¹⁰ nuclei are beta radioactive and decay in the following way:

$$_{47}Ag^{108} \rightarrow {}_{48}Cd^{108} + e^- + v^-$$

half life ~ 2.3 minutes
 $_{47}Ag^{110} \rightarrow {}_{48}Cd^{110} + e^- + v^-$
half life ~ 24 seconds.

The rapid decrease in the counting

rate after the activated silver foil is placed in front of the Geiger counter is due to the decay of the Ag^{110} activity whereas the slower fall off which remains is due to the Ag^{108} .

Exponential Decay and Half Life

The expression 'half life' deserves some further discussion. Radioactive decay is what is known as a statistical process; this implies that the probability of an individual radioactive nucleus disintegrating in a given short time interval is merely proportional to the duration of the interval and is quite independent of the time that has elapsed since it was formed by neutron capture or by any other process. Thus if we had a constant number of radioactive nuclei in a source the number of disintegrations per second, or activity, would be constant. However, the fact that some nuclei are decaying causes a reduction with time in the number of radioactive nuclei in the source and thus a reduction in the activity of the source. The activity decays away and, of course, so does the counting rate of the Geiger. This decrease turns out to be exponential and is plotted in Figure 7 for a source of In116 which gave an initial counting rate of 1200 counts per minute. The half life is the time during which the activity reduces by a factor of two, and in the particular case of In¹¹⁶ in 54 minutes. In the case of silver we had two exponentials superimposed, a very fast one with a half life of 24 seconds and a relatively slow one of 2.3 minutes.

For completeness we can activate a foil of Indium in our neutron source and though it will not have decayed appreciably by the end of the lecture it will be possible to see a decrease.

In summary we see that nuclei which have had an extra neutron added as a result of irradiation are often unhappy and try to change this neutron into a proton. This is beta radioactivity and is accompanied by the emission of an electron and an antineutrino. It is a relatively slow process, and the activity of a radioactive source containing such nuclei decays away exponentially with a half life characteristic of the particular type of nuclei. The resulting nuclei are often left in excited states and proceed to decay to their ground states by the emission of gamma rays. This decay also follows the exponential law but the half lives are usually much shorter than those of the preceding beta decay pro-

Use of Radioactivity for Nuclear Structure Investigations

What use has been made of this beta radioactivity? Many well known prac-

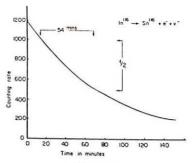


Figure 7
The exponential decay of the activity of a source of In¹¹⁶. The half life is 54 minutes.

tical applications come to mind immediately - the treatment of cancer with gamma rays from Co60, industrial radioagraphy of welds in large tanks and in pipe lines, the control of chemical processes with radioactive tracers, the measurement of paper thicknesses by its absorption of electrons from beta decay, etc. I will not dwell on these practical applications but instead, since I am a nuclear physicist, will try to tell you a little about its use as a tool in unravelling the structure of nuclei. I will also try to demonstrate a typical type of experiment in which radioactivity is used for this purpose.

Figure 4 gives a rather crude and oversimplified picture of the events following the beta decay of a Cono nucleus. The energies of the emitted gamma rays, in this case 1.7 MeV and 1.33 MeV, give information about the energy levels of the proton orbits inside the Ni⁶⁰ nucleus and are important pieces of evidence in attempts to understand what happens inside nuclei. A large number of similar experiments made on different types of nuclei can help physicists to formulate ideas on the structure of nuclei and have, indeed, been extremely useful and important in such research. Clearly a prerequisite for such experiments is a detector which can measure the energy of gamma rays; the Geiger counter can detect them but does not distinguish between those of different energies. One such detector is called a scintillation counter and will be used in our demonstration.

Scintillation Counter

It consists of a single crystal of sodium iodide which is mounted in a sealed container on the front face of a photomultiplier. The particular one for our demonstration has a diameter of 3

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inches and a length also of 3 inches; but they can be readily obtained in all sizes up to about 6 inches by 6 inches. Figure 8 shows a schematic diagram of the assembly. When a gamma ray is incident on the crystal it may knock an electron out of an atom of Na or I. In many cases the electron is knocked out as a result of a scattering of the gamma ray but in some cases the gamma ray is totally absorbed by the atom and the electron takes practically all the energy. Exactly the same thing, of course, happens in the metal walls of the Geiger counter but whereas the electron then merely initiates a standard discharge in the gas of the Geiger tube, its effect in the NaI crystal is quite different. In a rather complicated and not completely understood way it gives rise to a flash of light whose intensity is directly proportional to its energy. Hence the term 'scintillator' is often applied to such a crystal. Thus, if one can measure the intensity of this light flash, it will be a measure of the energy of the initial gamma ray. This is done by the photomultiplier which consists of a photocathode and a series of electron multiplying surfaces or dynodes. The photocathode emits a number of electrons and this number is proportional to the intensity of the light incident on its face. They are of very low energy and are accelerated to the first dynode where each one will knock out about 10 new electrons which in turn are accelerated to the second dynode. A very large number thus arrive at the final 'anode' but their number is proportional to the initial number emitted by the photocathode and hence to the intensity of the light flash in the scintillator. Consequently the height of the output pulse is proportional to the energy of the gamma ray.

One can summarize by saying that a scintillation counter consists of a scintillator which converts the gamma ray into a flash and a photomultiplier which gives out a pulse proportional to the flash. The device thus not only records the arrival of a gamma ray but also, by the height of the pulse produced, indicates its energy.

Kicksorter or Multichannel Analyzer for Data Recording

To record the information provided by the scintillation counter a simple scaler is no longer sufficient — we need a device to separate the pulses into different channels according to their height and then to count the number in each channel. Such a device is called a 'kicksorter' and consists basically of an electronic memory which stores each pulse in a compartment appropriate to its height. A 400 channel kick-

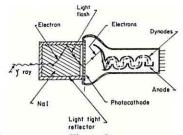


Figure 8
Schematic diagram of a typical scintillation counter.

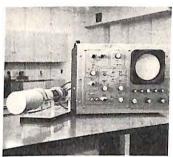


Figure 9
A 3-in.x3-in. NaI scintillation counter
and a 400 channel kicksorter.

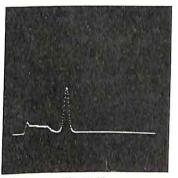


Figure 10

The spectrum of the gamma rays from Cs¹³⁷ obtained with the equipment shown in Figure 9.

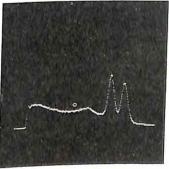


Figure 11
The spectrum of Co⁶⁰.

sorter, such as the one used for these demonstrations, has 400 compartments and each compartment can store up to about 10,000 pulses. These compartments are arranged so that each one corresponds to a slightly larger pulse height than the preceding one; consequently the pulse corresponding to an energetic gamma ray will be stored in a higher compartment or 'channel' than that corresponding to a lower energy gamma ray. Figure 9 shows the 'kicksorter' and scintillation detector.

The memory will store the pulses for as long as one wishes but can, at the throw of a switch, be 'examined' by a special circuit which displays its contents on a cathode ray tube. This is most readily described in connection with Figure 10 which is a picture of the screen of the kicksorter used in the demonstration. The scintillation counter had been looking at the gamma rays from a source of Cs137, a beta radioactive nuclide which decays into Ba137*. The excited state of Ba137 then goes to its ground state by the emission of a single gamma ray of 0.662 MeV. The compartments or channels increase in energy from left to right and the height of the spot is proportional to the number of counts received in that channel during the counting period or time that the memory was accumulating information from the detector. The prominent peak near the centre of the screen corresponds to the 0.662 Me V gamma rays emitted by the Cs137 source and actually due to the de-excitation of the Ba137 excited states. The peak is not concentrated in one channel, even though all the gamma rays have the same energy. This is due to many causes and indicates that the scintillation counter, though much more useful than the Geiger counter, is still not perfect. Recently, a new type of detector making use of a piece of germanium semiconductor into which some lithium has been introduced has been developed and is capable of providing a much better 'resolution'. Because of the complexities of the equipment associated with this type of detector it was not demonstrated in the talk.

If we put a source of Co⁵⁰ near our scintillation counter we get the 'spectrum' shown in Figure 11; the two peaks corresponding to the gamma rays of 1.17 MeV and 1.33 MeV are clearly visible. The spectrum from Mn⁵⁴ is shown in Figure 12 and again the gamma ray is a different energy from those we have seen with other sources. In each case, however, they give information about the different energy states in nuclei and hence about nuclear structure. The situation is analogous to optical spectroscopy where the wavelength of the emitted light from excited atoms

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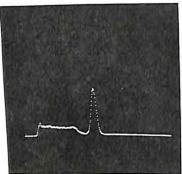


Figure 12 The spectrum of Mn 14.

is directly related to the energies of the

electron configurations in atoms. Wave-

lengths, A, are directly related to en-

ergies, E, by the simple equation E =

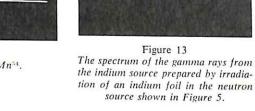
hc/λ where h is Planck's constant and

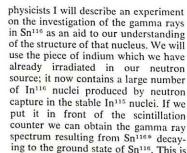
c is the velocity of light; the energies of

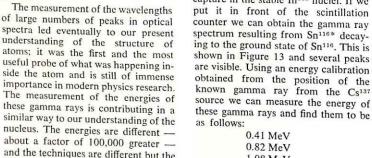
the two well known D lines of the

Sodium optical spectrum are close to

2.1 eV.







1.08 MeV 1.27 MeV 1.49 MeV (weak)

If we had extended the scale of our kicksorter and looked carefully we would have also found gamma rays at 0.14 MeV and at 2.09 MeV. One can

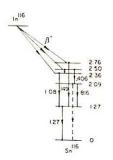


Figure 14 Decay scheme of In116 and energy levels of Sn116.

atoms; it was the first and the most useful probe of what was happening inside the atom and is still of immense importance in modern physics research. The measurement of the energies of these gamma rays is contributing in a similar way to our understanding of the nucleus. The energies are different about a factor of 100,000 greater and the techniques are different but the ideas are similar.

Experiment on Nuclear Energy Levels

To end this discussion of radioactivity and its uses to the nuclear fit these gamma rays into a 'decay scheme' for In116 shown in Figure 14. In 116, produced by neutron capture in In115, is represented by the short horizontal line at the top left and its beta decay is shown by the three slanting lines leading to three different excited states of Sn¹¹⁶ at 2.36, 2.50 and 2.76 MeV. The subsequent gamma decays of Sn116* are represented by the vertical lines which lead finally to the ground state of Sn116, indicated by 0. The excited states of Sn116 are seen to have energies of 1.27, 2.09, 2.36, 2.50 and 2.76 MeV.

This simple experiment performed in a relatively short time has thus given information about the energy levels in a complex nucleus. It is one of the techniques used by nuclear physicists to explore nuclear structure and is essentially the nuclear analogue of optical spectroscopy. Optical spectroscopy led to a detailed understanding of the atomic structure; nuclear structure is not yet so well explored but nuclear spectroscopy is providing much of the data which, we hope, will lead to a more complete understanding.

A Convenient Radioactive Half-life Experiment

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The choice of a suitable half-life experiment for student training and demonstration presents some problems. The half-life should be short, the materials cheap and relatively innocuous, and the radiation should be easily detectable on fairly simple, robust equipment. Preferably, the student should be able to repeat the experiment within a laboratory period.

Cheapness and lack of hazard have usually directed attention to the early members of the $^{238}\mathrm{U}$ (4n + 2) series of natural radioactivities. Uranium salts are commonly available in most chemical laboratories.

A well-known training experiment that has the merit of including an exercise in carrier precipitation is the separation of 234 Th from ²³⁸U by precipitation of ferric iron in a solution of uranium complexed by sodium carbonate. The ferric precipitate carries down thorium nuclides quantitatively and the radioactivity of the precipitate is followed by source-mounting or liquid-counting techniques. The activity of the milked carbonate solution can also be followed to show the growth of ²³⁴Th. The ²³⁴Th half-life of 24·1 days is too long for convenience. In the above experiments on the ²³⁸U-²³⁴Th relationship, the strong beta radiation ($E_{
m max}=$ 2·31 meV) from ^{234m}Pa (half-life 1·175 min; 70.5 sec), the short-lived daughter of ²³⁴Th, is measured since it is in secular equilibrium with the ²³⁴Th. (See Fig. 1). The ²³⁴Pa/ 234mPa branching ratio has been found to be 0.18 ± 0.02 per cent. Examination of the decay scheme suggests the separation of 234mPa from a 234Th preparation, and several 'milking' experiments using suitable 234Th 'cows' have been published.2-9

Solvent extraction is attractively fast and

makes limited demands on student dexterity. We have chosen this technique because it enables a closed regenerative system to be devised where only Pa nuclides are extracted from an aqueous uranyl solution into a ketonic solvent laver. The decay of 234mPa can then be followed by directing a detector towards the solvent layer. Neither uranium nor thorium is appreciably extracted by di-isopropyl ketone (DIPK) while the extraction of Pa shows a flat maximum close to 100 per cent for molarities of HCl in excess of To ensure reliable extraction the aqueous phase is made 7-8 M in HCl.

Procedure

(a) Apparatus and reagents

The two phase system is sealed in 8 in × 1.2 in pyrex tubing; the wall thickness is 1.6 mm. The vessel easily holds 100 ml, leaving sufficient space for complete and rapid mining of the two phases by shaking.

Laboratory-reagent grade uranyl nitrate hexahydrate (U.N.H.) and uranyl acetate are readily available and these are converted into uranyl chloride by repeatedly boiling down with concentrated hydrochloric acid. (Some silica may be precipitated.) The acid concentration is then that of the azeotrope and an equal volume of concentrated hydrochloric acid is added to yield a solution approximately 8M HCl. Solutions with 1.1 g uranium/ml are stable over several months at 20°C and this quantity of uranium is comfortably sufficient to give initial counting rates of 100 counts/sec. After addition of the DIPK the tube is sealed. Soon after shaking, the ketonic solvent develops a brown colour which gradually darkens. Substitution of a fresh solvent

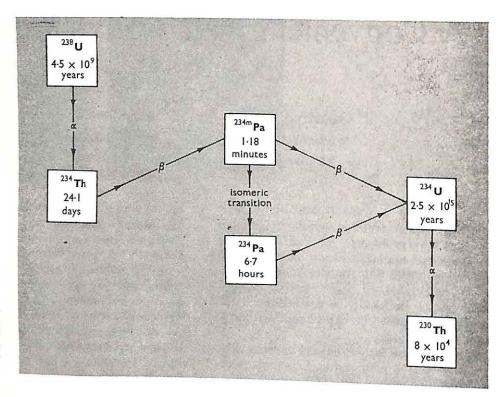


Fig. 1. Halflives of and decay scheme for uranium, thorium and protactinium.

layer gives the same result. There is no impairment of the radiochemical efficiency of the device. Tests on the uranium uptake into the solvent layer showed that 0.03 g U was extracted from an aqueous phase containing 46.5 g U (<0.1 per cent extraction). Iron present as impurity in the uranium salt or, more likely, the hydrochloric acid, is of course extracted under these conditions. Approximately 15 mg Fe was extracted from an aqueous phase containing 80 g U.

It should be noted that uranium salts are more toxic than arsenic compounds.

(b) Detecting and recording radiation

End-window Geiger detection is most commonly available and is suitable for this experiment. The window diameter of the Mullard MX 108, or its replacement MX 168, is 17 mm and this dimension dictates the depth of solvent required (20 ml). If the geometry of the arrangement permits radiations from both phases to enter the window of the Geiger confused results will be obtained. Arrangements are made with clamps so that the tube holding the two phase system can easily be replaced repro-

ducibly in position with respect to the Geiger tube.

The Geiger window (2·5-4·0 mg/cm²) causes negligible additional absorption of the beta radiation concerned. But a second glass tube of diameter 1·4 in and wall thickness 1·95 mm slipped over the containing vessel reduces the activity recorded by a factor of 15.

The overall efficiency of the device based on the total disintegration rate available is, as expected, very low (approximately 0.025 per cent). The extraction into solvent is very high but self-absorption in the solvent source means that only a thin layer of solvent contributes through heavily absorbing glass.

A further possibility is to arrange a dipping Geiger tube as a permanent insert such that it dips only into the solvent layer. The large increase in detection efficiency should showup a residual response due to ²³⁴Pa (UZ), 6.7 h half-life, after the ^{234m}Pa (UX₂) has decayed.

A ratemeter can be used with time constants of 1, 5 and 25 sec. The longest of these is then used to establish a reliable background count before extraction. The

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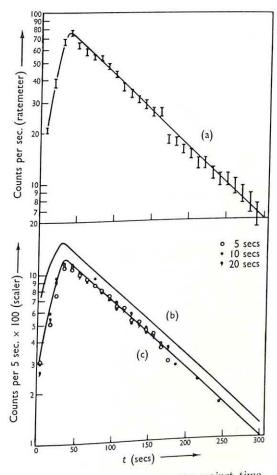


Fig. 2. Typical plots of count rate against time. decay of 71 see half-life can be followed using the 5 sec. setting. The proper selection of time constant by the student is a useful elementary exercise in the statistics of counting procedures. The rate of arrival of pulses is averaged over an effective interval of 2RC where RC is the time constant. This means that

 $S \text{ rate} = \sqrt{\frac{r}{2RC}}$

where S rate is the standard deviation of the rate r, measured in events/unit time.

The maximum count rate is in the region of 130 counts/sec. It is convenient to avoid changing scale during a run and to start timing with the ratemeter indicating 100 counts/sec. A quench unit is not necessary. The dead-time of the MX 108 is 100 microseconds giving a 'true' count rate of 101

counts/sec. for a measured rate of 100 counts/ sec. The excellent values of the half-life obtained confirm that a coincidence correction is not important over the range used.

It is possible, but energetic, to use a scaler instead of a ratemeter for registration of counts. A 10-sec. counting period taken once every 20 sec. can be used and the count obtained ascribed to a time corresponding to the mid-point of the counting period. Students may discuss the validity of this treatment. (It is also possible to use 5 sec. counting periods). A chart recorder is, of course, very useful.

Results

Figure 2, curve (a) shows a typical plot of count rate (using a 5 sec. time constant) versus time in seconds since the end of shaking. The initial growth in activity corresponds to the separation of the solvent layer into a clearly defined source at the top of the vessel. Subsequently simple decay is followed with a half-life of 71 \pm 1 sec. This is in good agreement with the accepted figure of 70.5 sec.11 After many repetitions the slope is found to be consistent and the same low background (2 counts/sec. for the unshielded MX 108 levelled at the solvent layer) is obtained 15 min after shaking. This confirms that a negligible amount of 234Th is extracted into the solvent layer. Curve (a) refers to a shaking time of 30 sec. The only detectable variability in data arises from variation of geometry in replacing the extraction vessel after shaking. The extraction system used for this data had an aqueous phase of 62 ml of 7-8 molar HCl containing 62 g uranium (1.00 g U/ml) and a solvent layer of 20 ml DIPK.

Curve (b) is a plot of similar data, for a 30 sec. shaking time on the same system, registered on a scaler by a different end-window geiger tube. Counts are taken for 5 sec. in each 10. This gives a good decay curve and affords a comparison with curve (c) which relates to a set of data obtained by the same scaler technique for an extraction system containing an aqueous phase of 80 ml of 7–8 M HCl containing 46.5 g uranium (0.58 g U/ml) and a solvent layer of 30 ml DIPK. To enable the distribution of points

to be shown round curve (c), the distribution round curve (b), which is quite similar, has been omitted. Curve (c) is a smooth fit to data relevant to 15 sec. shaking. The procedure can be repeated for shaking times of 5, 10 and 20 sec. and the points for these are shown around curve (c). The distribution round curve (c) shows that variation of shaking time over this range has no detectable effect. The time of shaking can be extended to 60 sec. without any significant change in results, provided that care is taken to ensure reproducible geometry.

Lower counting rates would be expected for the device with a lower uranium content. The reason that the peaks for curves (b) and (c) occur at about the same time after shaking stopped (40 sec.) is not readily explicable since several factors are involved. The peak time indicates the time necessary for the emulsion produced on shaking to clear, so that only solvent is in line with the geiger window.

Viscosity effect

However, it appears that with increased viscosity of aqueous phase (increased uranium content), the time to reach the peak increases. One of the mixtures, for example, has a saturated aqueous phase which is very viscous and the peak time is as long as 80 sec. This period is lost to the study of the decay. However, a usefully high peak count rate (approximately 100 counts/sec.) is obtained because the uranium content is high.

A brief investigation of this factor was carried out with a vessel which had not been sealed off. Initially 70 ml of a 7-8 M HCl aqueous solution containing 74.5 g uranium were placed in the vessel with 30 ml DIPK. After shaking, the volumes were: 62 ml aqueous phase: 38 ml DIPK phase. The uranium content of the aqueous phase was now 1.20 g uranium/ml. A peak count rate of 43 \pm 2 counts/sec. occurred 60 sec. after shaking. The solvent layer was then reduced to 20 ml and the corresponding curve had a peak of 62 ± 3 counts/sec. reached in 65-70 sec. after shaking. Finally, 10 ml of the aqueous phase were replaced by 10 ml of aqueous 8 m HCl. The uranium content was now 1.00 g/ml. This system

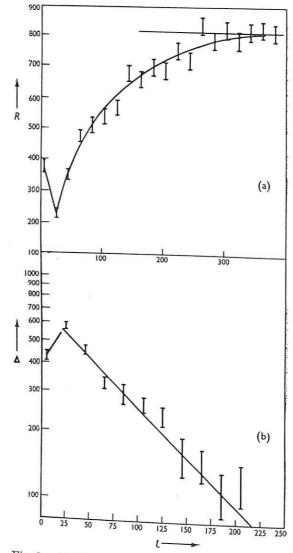


Fig. 3. (a) Plot of 10 sec. counts against time after shaking, using scaler technique; (b) semi-logarithmic plot of Δ against time.

also gave a peak of 62 ± 3 counts/sec., but this was reached in 50 sec.

In another mixture (0.58 g U/ml) when the solvent phase was increased to 40 ml, peaks for all shaking times in the range 5-60 sec. occurred 20-25 sec. after shaking ceased. The peak count rate was 42 ± 2 counts/sec. With 30 ml of solvent all peaks occurred at 40 sec. after shaking (see curve (c) Fig. 2). Increase of volume of extracting solvent beyond the Geiger's diameter reduces the count rate registered. However, if the Geiger is levelled at the top of the solvent,

less time is required to obtain peak count rate since clear solvent is obtainable earlier.

The growth in 234mPa activity of the extracted aqueous phase can be followed by directing the Geiger window at the lower phase after shaking. The count rate drops to a minimum as the DIPK droplets rise carrying the extracted ^{234m}Pa, leaving a clear aqueous phase. The aqueous phase contains practically all the 234Th parent from which the equilibrium amount of 234mPa can grow. Figure 3a shows a plot of 10 sec. counts versus time after shaking, using the scaler technique. Ten second counts were taken every 20 sec. and the values credited to a time midway in the counting period. Because of the larger volume of aqueous phase, the growth curve cannot be as precise as the decay curves in the above system. This is reflected in Fig. 3b where the difference $\Delta = (a_1 - a_t)$, where a_1 is the observed activity of the lower layer before shaking and a_t is the value t seconds after shaking, is plotted against time on a semilogarithmic plot. This difference, Δ , decreases with a half-period of 71 sec. as one would expect but the standard deviations shown make the plot clumsy. However, it completes the analysis of secular equilibrium.

This experiment has been used successfully

over several years.

Conclusions

- 1. A system made up of 80 ml of aqueous 7-8 M HCl containing about 1 g uranium/ml, extracted by 25 ml of solvent layer (DIPK) gives a ratemeter response in excess of 100 counts/sec. This conveniently enables a timer to be started when the reading is fullscale at 100.
- Five seconds of shaking establishes Further shaking extraction equilibrium. simply ensures that any 234mPa born in the aqueous phase is extracted to replace that decaying.
- The time for the emulsion created by shaking to settle is independent of shaking time in excess of 5 sec.
- Fifteen minutes after equilibrium a further shaking can be initiated to repeat the experiment.

5. Growth of activity of the aqueous phase can be followed to complete the analysis of secular equilibrium.

Acknowledgments

Thanks are due to Mrs P. R. Hoare for assistance with the experiments and to Mrs V. A. Buckle who drew the figures.

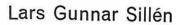
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Who controls the past controls the future Who controls the present controls the past

Ignorance is strength G Orwell, 1984





How have sea water and air got their present compositions?

The present

The ocean is wide and deep: its total area, 361×10⁶ km.² covers 71 per cent of the total area of the Earth, and its average depth is 3·8 km. Indeed, a globe representing the Earth on the scale 1:20 million would have a diameter around 64 cm.: the ocean, on the same scale would be 0·2 mm. deep, so that the globe would feel definitely wet on the outside.

The volume of the ocean is estimated as $1\cdot37\times10^{21}$ l, which may seem a great deal to a chemist; so in the following we shall often consider the fraction $1/(1\cdot37\times10^{21})$ of the real system, that is one litre of sea water and the corresponding amount of air and sediments.

For instance, knowing the weight of the atmosphere and the volume of the ocean, one finds that for every litre of sea water there is, in the atmosphere, 0.1010 mole N₂, 0.0271 O₂, 0.0012 Ar, and 0.000039 mole CO₂, *i.e.* a volume of around 3 litres at 1 atm. and 10°.

Table I gives the main constituents (and some minor ones) in 1 kg. of sea water at a salinity of 3.5 per cent, which is close to the average.² Because of evaporation or

TABLE I

THE MAIN CONSTITUENTS (AND SOME OTHERS) IN MOLES/KG. SEA
WATER (~0.975 l.) AT 3.5 PER CENT SALINITY (=35 g. DISSOLVED

SALTS PER KG. SEA WATER)

H ₂ O Na ⁺ Mg ²⁺ Ca ²⁺ K ⁺	53·557 0·4680 0·0532 0·0103 0·0099	Sr ²⁺ Cl- SO ₄ ²⁻ HCO ₃ - Br-	0·0001 0·5459 0·0282 0·0023 0·0008	N ₂ O ₂ NO ₃ -	0·0001 0·0004 0·0006 0·0004 0-35×10-6 0-2·3×10-6
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This article is based on a Centennial Lecture to The Chemical Society delivered last January by Professor Sillén of the Royal Institute of Technology, Stockholm 70, Sweden.

addition of fresh water, the salinity of the surface water may vary from $3\cdot 4$ to $4\cdot 0$ per cent between various places in the open sea, and the concentrations of various ions in mole/kg. sea water vary correspondingly. However, the ratios between various ions, e.g. Na+: Mg²+, and the pH value, pH = $-\log [H^+] = 8\cdot 1 \pm 0\cdot 2$, are quite constant in the open sea. Moreover, there are no strong reasons to think that pH, or ionic ratios, have varied very much over the last few hundred million vears.

This is quite remarkable since the non-volatiles in sea water are a very small fraction of the Earth system. Converted to oxides, they could cover the Earth's surface by a uniform layer of only ~ 20 m. thickness³ whereas the sediments are measured in thousands of metres and the radius of the Earth is about 6.400 km.

Chemical interaction

There is a continual chemical interaction between the sea and the rest of the Earth's crust. Water from the ocean evaporates, comes down as rain and attacks the rocks and the soil. The rivers carry with them dissolved ions and suspended solids which may interact with sea water, and sediments are formed, especially on the continental shelves. However, they do not remain there for ever. As is well-known many of the Earth's highest mountains are old marine sediments, e.g. the Alps and Himalayas. Now and then, the earth's crust wrinkles a little, and new mountains shoot up where there was earlier sea.

To discuss the addition of matter by the rivers to the sea, we may use the unit, mole per cm.² of total Earth surface. Table II gives³ the amounts of ions in the present ocean, and the amounts of dissolved ions added by rivers in 100 million years, using the estimates of Garrels and

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Mackenzie⁴. Most of the chloride and sodium probably represents sea spray that is being washed back by rivers, but the other ions must largely result from attack on rocks or soil. The amounts added are usually much greater than those present in the sea. In addition, there are suspended solids which, by different estimates, may be somewhere between 250 and 640 kg. per cm.² in a 100 m. years. These solids are to a great extent clay minerals, which can interact with sea water by ion exchange or by phase transformation. For instance, 1 kg. of kaolinite or mica is equivalent to 2·5 mole H+ or K+ by reaction (2), see p. 294. These were the additions in 100 m. years (at least as an estimate of the order of magnitude), and we must remember that the sea has probably existed for more than 2,000 million years.

There are other types of chemical interaction too: underwater volcanism, life processes, metamorphism, additions by dust and rainfall and reactions accompanying the rise and submergence of land.

So we may well ask: how could the ocean keep a roughly constant composition?

Table II

PRESENT AMOUNT OF IONS IN SEA, AND AMOUNT OF DISSOLVED IONS ADDED BY RIVERS IN 100 MILLION YEARS⁴ IN MOLES PER CM.² OF TOTAL EARTH SURFACE

	Na+	Mg ²⁺	Ca ²⁺	К+	Cl-	SO ₄ 2-	CO ₃ ²⁻	NO ₃ -
Present in ocean Added in	129	15	2.8	2.7	150	8	0.3	0-01
100 m. years	196	122	268	42	157	84	342	11

The past

According to the now prevalent 'cold' theory of planet formation, the Earth like the other planets was formed by the agglomeration of cold particles. The original surface of the Earth may have looked something like that of the moon, with craters from the last additions of large lumps of matter.

The decay of radioactive atoms inside (K, Th, U) increased the temperature of the interior, and eventually there were chemical transformations and partial melting. Matter was redistributed by gravitation and volatile substances distilled towards the surface. The volatiles were presumably the same ones that are still ejected by volcanoes: H₂O, HCl, CO₂, compounds of S, B, N, F etc.

Unlike the moon, the Earth was heavy enough to keep a great part of the volatiles within its gravitational field: they reacted with the solids they met and so in due time the sea resulted, with H_2O , S and Cl from the volatiles, and Na, Mg etc. from the rocks.

The components. The geochemical balance

In 1933, V. M. Goldschmidt⁵ tried to make up a balance, 'the geochemical balance', for this reaction igneous rock + volatiles → sea water + sediments + air (1)

assuming that there had been a one-way reaction. He knew the composition of sea water very well, and the average composition of igneous rock fairly well for the major elements. For the sediments (much of which are in the sea) his figures had to be sketchy. His conclusion was that for each litre of sea water, about 600 g. of igneous rock had been decomposed, forming an approximately equal amount of sediments.

JULY

Several attempts have been made to refine the balance. The most recent one is that of M. K. Horn,⁶ who had available more accurate data for a much larger number of elements. Horn suggested that about 1·2 kg. of igneous rock had been decomposed per litre of sea water.

Table III gives the balance for the major elements, recalculated to the unit, mole/litre sea water. Where two numbers are given, the first is due to Goldschmidt, the second to Horn. Either set is consistent, as is seen by comparing the total, for a given component, under 'from' (sum of columns 2 and 3) and under 'now' (sum of columns 4, 5 and 6). The estimates of volatiles (column 3) appear as a difference, but otherwise the numbers are fixed by the ratios assumed between the amounts of the various types of sediments and igneous rocks—altogether around five parameters—and the known average chemical analyses. It is a remarkable fact that Horn could achieve a balance for about 60 non-volatile elements, and this could be taken as a proof for the correctness of the underlying assumption of a one-way process (1).

However, there are strong reasons to assume that reaction (1) also goes in the reverse direction. For instance, in the earthquake belt around the Pacific it seems that the ocean floor is moving down underneath the continent, and a new ocean floor is rising at the mid-Pacific ridge. Both movements are of the order of cm. per year. As the sediments and trapped water descend to regions with a higher temperature, sodium and magnesium from the sea water reacts with clays etc. to form new igneous rock, whereas the volatiles are set free and pass out through the volcanoes which are conveniently placed above. A reversal of (1) can also result from sediments and trapped sea water sinking vertically to hotter regions.

There are some who will think that practically all the igneous rock we see is old sediments, and that matter has been through on the average perhaps ten or 20 such cycles in geological time.

I recently made calculations on a recycling model? where the volatiles in the ocean etc. are continuously attacking two types of igneous rock: basaltic (mostly on the sea floor) and continental. The reaction products—sediments—are continuously being carried back to depths where igneous rock of both types is being formed. If one sets up the mass balance equations, and inserts the conditions for a steady state, the same mathematical expression is obtained as the balance condition for the one-way reaction. So the agreement in the geochemical balance can be explained, either by a one-way process (1) or by a two-way process (1) that has come to a steady state. In either case, Table III would give under 'from' or 'now' the number of moles of each component that are present in the

Table III

BALANCE OF MATERIALS FOR THE FORMATION OF ONE LITRE OF SEA WATER, CALCULATED FROM THE ESTIMATES OF V. M. GOLDSCHMIDT⁵ and M. K. HORN⁶ IN MOLES

		From		Now			
		Component Primary rock Volatile		Air 1 1			
H₂O Si	(SiO ₂)		6064000	54-90			Sediments
H₂O Si Al Cl Na Ca Mg	(AlO _{1.5} , Al(OH) ₃) (HCl) (NaO _{0.5} , NaOH) (CaO, Ca(OH) ₂)		6.06/12·25 1.85/3·55 0.01/0.02 0.76/1.47 0.56/1.09	0.54/0.94		54·90 0·55 0·47	6.06/12.25 1.85/3.55 /0.40 0.29/1.00
K C	(MgO, Mg(OH) ₂) (KO ₀₋₅ , KOH) (CO ₂)		0.53/0.87 0.41/0.79 0.02/0.03 0.02/0.03	0·60/2·06 0·53/1·05		0·01 0·05 0·01 0·002	0.25/1.00 0.55/1.08 0.48/0.82 0.40/0.78 0.62/2.09
O ₂ Fe	(FeO, Fe(OH) ₂) (FeO _{1,5} , FeOOH)		0·55/0·91 0·32/0·53	0·07/1·01 0·027/0·022	0.027/0.022	0.002	0.55/1.08 0.07/1.01 0.55/0.91
Ti S F P	(TiO ₂)		0·23/0·38 0·06/0·12 0·01/0·02 0·03/0·05	0.06/0.06		0.03	0·18/0·32 0·37/0·59 0·06/0·12
Mn N ₂	$(MnO_{1 \text{ to } 2})$	** **	0·02/0·04 0·01/0·05	0-101/0-082	0-101/0-082	0 03	0·04/0·05 0·03/0·05 0·02/0·04 0·01/0·05

fraction $1/(1\cdot37.10^{21})$ of the system (sea water + sediments + air).

How then is the composition of the sea kept stable? Reaction (1) may be called an acid-base titration, the acids coming from the volatile substances, and the base (NaOH etc.) from the igneous rock. So we can ask why did that acid-base titration result in the pH we now have?

The equilibrium model (an imaginary experiment)

In an attempt to understand what reactions could stabilize the composition of sea water, I have suggested an imaginary experiment.^{1,8} Let us represent the *real system* by one litre of sea water and the corresponding amount of air (~3 litres) and sediments (0.6 kg. according to Goldschmidt⁵ or 1.2 kg. according to Horn⁶). It contains the numbers of moles of the major components given in Table III and in addition all the minor elements.

The equilibrium model is an imaginary system which contains the same components as the real system, in the same amounts, but in which a state of true equilibrium has been reached. One may build it up by adding one component after another and stirring until equilibrium is reached. We shall now consider two stages in the build-up of this model.

Five-component system, HCl-H₂O-SiO₂-Al(OH)₃-KOH. This may be called a simplified ocean model: the two first components correspond to the volatiles, and the others to the oxides in igneous rocks. It has been simplified since compounds of C, S, Na, Ca, Mg, Fe etc. have been left out. However, even this simplified ocean model may have some characteristics that make it easier to understand how the real system could be stabilized.

If these five components are mixed in ratios around those in the real system, three solid phases are stable: quartz, SiO₂; kaolinite, Al₂Si₂O₅(OH)₄; and K-mica, KAl₃Si₃O₁₀

(OH)₂. Let us consider a system (Fig. 1) consisting of these three solid phases, a gas phase (chiefly water vapour) and an aqueous solution containing the ions H⁺, K⁺ and Cl⁻.

Applying Gibbs phase rule to this system, the variables to be considered are pressure p, temperature T, ionic concentrations $[H^+]$, $[K^+]$ and $[Cl^-]$, and the minute concentrations of whatever species of Al and Si the solution may contain. The phase rule states that the system has 5 (components) +2-5 (phases) =2 degrees of freedom. It seems most practical to use T and $[Cl^-]$ as the controlled variables, since Cl^- cannot leave the solution. The phase rule then states that once T and $[Cl^-]$ have been chosen, then p and the concentrations of K^+ , H^+ etc. are fixed by the equilibrium conditions.

To understand this result better we may apply the equilibrium law (for brevity in its simplest form, without

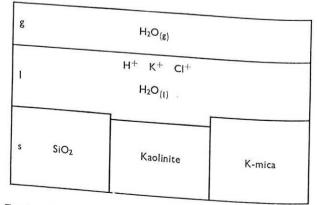


Fig. 1. Equilibrium in five-component system with gas phase, solution and solid quartz, kaolinite and K-mica

activity coefficients). We may consider the reaction between kaolinite and K-mica

$$\begin{array}{ll} 1{\cdot}5\;{\rm Al_2Si_2O_5(OH)_4(s)} + {\rm K}^+ \rightleftharpoons \\ & {\rm KAl_3Si_3O_{10}}\;({\rm OH})_2(s) + 1{\cdot}5\;{\rm H_2O} + {\rm H}^+ & \dots \end{array}$$

The equilibrium condition gives

$$K = \lceil H^+ \rceil / \lceil K^+ \rceil \qquad \dots \qquad \dots \qquad \dots \qquad (3)$$

(2)

In addition we have the charge condition: equal amount of positive and negative charges per litre:

$$[K^+] + [H^+] = [Cl^-] + K_w/[H^+]$$
 .. (4)

The last term is $[OH^-]$. The equilibrium constants, K and K_w , are determined by T. If $[CI^-]$ is also fixed, there are two equations (3) and (4) between the two unknowns $[H^+]$ and $[K^+]$ which means that both are fixed. To the system in Fig. 1, one may add arbitrary amounts of HCl or of KOH(+KCl), and $[H^+]$ and $[K^+]$ will return to their original equilibrium values, as long as one keeps $[CI^-]$ and T constant, and lets no phase disappear completely. So, the system would be a pH-stat rather than a buffer.

This result might suggest that even in sea water, pH and the main ionic concentrations are determined by reactions similar to (2). After all, large amounts of clay minerals, among them kaolinite and mica, come into contact with sea water.

In 1959, when I made this suggestion, most of my audience did not understand what I meant, and those who understood did not like it. By then it was well known from all textbooks that the pH of sea water is determined by the buffering of $CO_3^{2-} + HCO_3^{-} + H_2CO_3$, and the silicates were thought to react so slowly that their main importance for sea water would be acting as walls of the container.

In the meantime, however, more has become known about the equilibria and reactions of clay minerals. For instance, two of the essential equilibria have been studied by Julian Hemley in the U.S.A.⁹ His data for the reaction (2), on extrapolation to 25°, give a figure somewhere between 10^{-6.0} and 10^{-6.5}, perhaps 10^{-6.4}. Now, the ratio in sea water is 10^{-6.2}, which is close enough to be interesting; one could not have expected exact agreement since after all sea water has an average temperature other than 25° and moreover the real system contains more components than the five-component system. In addition, real mica is a solid solution containing also, for instance, Mg.

For a similar equilibrium between kaolinite and mont-morillonite in a five-component system with Na, the ratio H+/Na+ also comes not far from that in sea water.¹⁰

Moreover, studies of the transformation of fresh-water clay on contact with sea water by Whitehouse and McCarter¹¹ and by other workers,¹⁰ indicate that most of the chemical transformation is completed within a day or two, and that new phases of sufficient grain size to be separated by physical methods have been formed after a separated by physical methods have been formed after a couple of years. For such reasons, some geochemists, couple of years. For such reasons, some geochemists, notably Robert M. Garrels¹² and H. D. Holland,¹⁰ have recently found the 'silicate theory' quite acceptable.

In a nine-component system HCl-H₂O-SiO₂-Al(OH)₃-NaOH-KOH-MgO-CaO-CO₂, we can assume again that

we have a gas phase containing H_2O and CO_2 , a solution with the major cations and Cl^- , and a certain number of solid phases. We may now ask the reverse question: what should the number of phases be to give the system two degrees of freedom? Once T and $[Cl^-]$ are fixed, all the other ionic concentrations and $p(CO_2)$ will then be given by the equilibrium conditions. The phase rule very simply gives the answer: 9 (components) +2-2 (degrees of freedom) =9 phases.

From the information available about silicate reactions and equilibria one may suggest as a working hypothesis¹³ that these nine phases would be: (1) gas phase, (2) aqueous solution (of composition close to sea water), (3) quartz, (4) kaolinite, (5) chlorite, (6) illite = hydromica, (7) montmorillonite, (8) phillipsite and (9) calcite, CaCO₃. All these minerals have been observed in large quantities in marine sediments, and all appear to be stable in contact with sea water, with the possible exception of phillipsite.

One would need more experiments on equilibria, and also studies of individual clay minerals separated from marine sediments, e.g. by electrophoresis in sea-water media, in order to judge the exact composition of the stable phases and compare them with what is really found. Such studies may lead to the replacement of phillipsite by some other mineral.³

If the equilibrium model resembles the real system, one would have a state like that in Fig. 2: [Cl-] is determined by the ratio HCl/H₂O in the volatiles delivered from the interior of the Earth, and pH and the main cationic concentrations are determined by equilibria with aluminosilicates.

Now, we can consider what influence carbonate has on the pH of the equilibrium model. If the component CO_2 were taken out from the system, we should have to remove solid $CaCO_3$, the little CO_2 from the atmosphere and the small amount of HCO_3^- from the solution. To preserve neutrality it would be necessary to adjust the cationic concentrations, but only by about 0.4 per cent. If the equilibrium model contains the phases suggested above, its pH and main cationic concentrations are hence mainly determined by the aluminosilicate equilibria, whereas $p(CO_2)$ and $[HCO_3^-]$ may be said to be indicators only. In the real system, admittedly, CO_2 and carbonates play an important role for transporting matter, and for making equilibration easier.

I have tried to calculate what would happen on addition of the remaining components, including the minor ones, to the equilibrium model: the solid phases at equilibrium in general turned out to be those really found in marine sediments. The concentrations sometimes agreed nicely, and sometimes gave food for thought to an inorganic chemist.¹

Do I really think there is true equilibrium in the real system, sea water-sediments-air? Certainly not: everything of interest in and around the sea comes from non-equilibrium processes: life, currents, changes in weather etc. All I claim is that the equilibrium model may be sufficiently similar to the real system to make a comparison interesting and a useful first approximation to the real system.^{1,8}

The air

Now let us turn to the air. Its main constituents are nitrogen, oxygen and argon. The argon can be dealt with very simply. It consists chiefly of 40Ar, unlike 'cosmic' argon, and has very probably been formed by radioactive decay 40K→40Ar. So, it was brought to the young earth in a solid state.

It seems likely that the original atmosphere of the Earth was practically free of molecular oxygen, O2, and that all we have has been formed later, especially by photochemical decomposition of H2O with subsequent loss of H2 to outer space, and by biological photosynthesis with subsequent burial of organically bound C, leaving excess O2 (Fig. 3).

On the other hand, oxygen is consumed by biological oxidation, by oxidation of \tilde{S}^{2-} and Fe^{2+} minerals, and in the last few centuries by industrial combustion. The consumption by oxidation of volcanic gases, especially H2, has been pointed out by Holland¹⁴. Since H₂ may be the result of the reaction of H₂O from the surface with iron(II) in the crust or the mantle, this process may however be equivalent to an oxidation of Fe in deeper layers.

Another imaginary experiment

One might like to speculate what was the composition of the atmosphere and the ocean in the earlier stages of our planet. To get some basis, I have tried to calculate what would happen if the 'equilibrium model' were reduced, e.g. by adding H₂.15,16 The various stages it passes through might resemble earlier states of the real system. As a measure of the oxidizing power of the system, I have used the quantity pE, which is high in oxidizing and low in reducing systems.

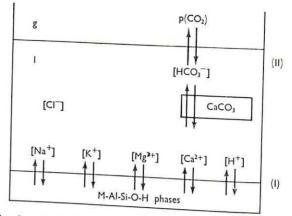
$$pE = -\log [e^-] \qquad .. \qquad (5)$$

The fundamental assumptions were that the concentration of Cl- is fixed, and that the concentrations of major cations, and pH = 8.1, are fixed by pE-independent

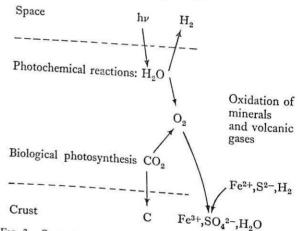
In the calculations the temperature was assumed to be 25°. If someone could tell more accurately what the average temperature of the Earth surface was, say 1,000 million years ago, it would not be hard to repeat the calculations for that temperature. At any rate, it seems hard to say whether it was hotter or colder than 25°-and there are very good tables of equilibrium constants available for 25°. As a check, I have made the corresponding

The results are indicated in Fig. 4^{16} which has pE on its horizontal scale. At the bottom scale are indicated the solid phases that could exist at equilibrium for the various pE. The vertical scale gives log c (concentration in the aqueous solution), or $\log p$ (partial pressure in the gas phase) for some important species that are influenced by pE.

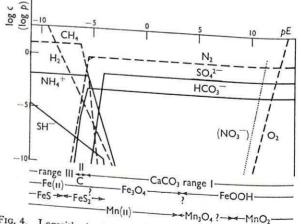
As pE is gradually decreased from the present value, 12.5, to lower (more reducing) values, the following will happen: O_2 (at present log $p(O_2) = -0.7$) disappears. S, at present in the equilibrium form SO42- ions in the ocean, is transformed to S2- in minerals. N is transformed from N₂(g) to NH₄ ions, perhaps to a large extent



Equilibrium in a nine-component system with gas phase, aqueous solution, solid calcite and aluminosilicate phases, according to a working hypothesis



Some important processes producing and consuming Fig. 3.



Logarithmic diagram showing log c (full-drawn lines) Logarithmic diagram showing log c (full-drawn lines) for dissolved substances, and log p (broken lines) for gaseous species in the 'equilibrium model', at various pE (degrees of reduction). The lower edge shows the stability ranges of some important solid phases. Species and phases that are not influenced by pE within this range are not given. 16

in aluminosilicates (replacing K+) but also in the solution. C is reduced from the present state, chiefly CaCO₃, via solid carbon to methane. Fe and Mn are reduced. At the lowest pE, free H2 appears. So, perhaps the ocean has always had roughly the same composition as now, whereas the atmosphere at one period may have contained chiefly N2 and earlier considerable amounts of CH4 also.

Probiotic soup

Many people have speculated on the possibility of the formation of life by random reactions of organic substances on the primitive Earth. Some scientists, notably Haldane in this country17 and Oparin in the Soviet Union,18 have suggested that the primaeval ocean contained quite high concentrations of organic substances: fatty acids, aminoacids, carbohydrates etc. The figure 10 per cent of organic substances has been mentioned, and if this were true, the primaeval ocean may well have deserved the name 'probiotic soup'.

Since it has been indicated that the organic compounds would be thermodynamically stable, it may be of some interest to see what the concentrations of various organic substances would be at real thermodynamic equilibrium. One might guess that their concentrations would increase with increasing reduction, i.e. decreasing pE. Indeed, for CH_4 , this is so: at very low pE, one would have a methane pressure around 10 atm. If there came from outer space an organism that knew how to synthesize organic material from methane it would have found very pleasant surroundings. Otherwise, CH4 seems to be a not too promising starting material for random organic synthesis.

For other organic substances, however, the largest concentrations seem to be reached somewhere in the region of pE = -5.5 or -6. They are not too impressive. The highest equilibrium concentration calculated for an organic species in the aqueous solution is that for acetate, CH₃CO₂-, which turns out to be around 10-9 M. The concentrations of amino-acids appear to be less than 10^{-20} M, that of glucose is about 10^{-90} M etc. 15 So, if the probiotic soup were restricted to the equilibrium concentrations in the ocean, it would have been a thin soup indeed. To me it seems easier to assume that relatively high concentrations of organic substances were reached in systems isolated from the ocean, like lagoons, shallow lakes, moist soil etc. Organic substances, formed by electrical discharges or photochemical processes could there find a chance to concentrate, and would even find catalytic surfaces and shelter from destroying u.v.-light.

Oxygen regulation

Goethite, FeOOH, is an important constituent of marine

sediments, and the reaction

12 FeOOH_(s) \rightleftharpoons 4Fe₃O_{4(s)} + 6H₂O_(a) + O_{2(g)} · · · goethite magnetite $K = p(O_2)$ (6)

might be of importance for the reduction-oxidation balance of our system. The condition for equilibrium between goethite, magnetite and an aqueous solution (6) is obviously

that the oxygen pressure be kept constant, and it might be interesting to calculate what this $p(O_2)$ would be.

I first did what perhaps most inorganic-physical chemists would be inclined to do: I calculated p(O2), first using the values for ΔG° etc. given by Latimer, ¹⁹ then using the values given in N.B.S. Circular 500.²⁰ From both sets of data I got the same value which was, within the uncertainty limit, equal to the present oxygen pressure in the atmosphere, 0.2 atm. This suggested a very simple mechanism regulating the oxygen pressure: first there was no oxygen at all, then O2 gradually built up by the processes in Fig. 3, and finally, when $p(O_2)$ in the atmosphere had reached the value corresponding to equilibrium (6), the oxygen pressure was kept constant while magnetite was gradually being transformed to goethite. This seemed an elegant explanation, and I was quite happy for about three

After that I looked into the primary data. I then found that there were several sets of experimental data in literature that one could combine to find K values (6). The good agreement between Latimer and N.B.S. came because they had selected the same sets of primary experimental data. However, by using another selection of primary data I could deduce other equilibrium pressures, which seemed equally well founded such as 10-36 or 10-117 atm.16 So, my present conclusion is not that the atmospheric p(O2) is regulated by the equilibrium (6) but rather that someone should look better at the thermodynamics of FeOOH(s) and Fe₃O_{4(s)}, especially the forms that may exist at equilibrium with aqueous solutions.

The nitrogen problem

If one tries to calculate the equilibrium concentrations of various nitrogen compounds, one will soon find that at the present pH and pE values, practically all nitrogen should at equilibrium be present as nitrate ions NO3- in the ocean. As a matter of fact, nitrate is being formed from N2 by Azotobacter and its relatives in the soil, and also in the ocean, and moreover nitrate, with some nitrite and ammonium ions, is formed by atmospheric reactions and carried down by rainfall.

Hence, there are large additions of nitrate to the ocean by rivers and rainfall. On the other hand, attempts to make a nitrogen balance21,22 have indicated that no reaction is known that would seem to balance the loss of N2 by a corresponding production. The most important $NO_3^- \rightarrow N_2$ process at present known seems to be the reduction of nitrate in some reduced regions on the sea floor, but this does not seem to be adequate. The present balances would indicate that within 50 million years practically all N2 would have been converted to NO3- in

The obvious conclusion is that there must be some process restoring the N2 but that it has hitherto been neglected. The simplest explanation that one might think of would be that there is an organism living close to the sea surface that can convert other nitrogen compounds, especially nitrate, to N₂, even in the presence of excess oxygen. 16 The biochemists I have asked (and they are quite a few) do not know of any such reaction, but surely an organism with this ability might keep its secret for a long while. The concentration of nitrate in the ocean is quite small (of the order of 35 μ M), smaller than that of N_2 (~1200 μ M N), and its action would be revealed only by small variations in the concentration of free N2. To determine it, one would have to make special experiments; for instance study whether various organisms can create N_2 in a solution, equilibrated with an Ar-O2 atmosphere. The explanation may be more complex involving a chain of biochemical reactions or many organisms, but still my guess is that if one wants to find the missing term in the nitrogen balance-and this is a real problem-then it is to the biologists and biochemists one should first go.

I do not pretend to have given a complete answer to the questions posed in the title of this paper, but perhaps I have shown how the problem can be broken down to a number of partial problems, most of which may be interesting to chemists. It may also be apparent that, in order to solve these problems, it will be necessary to have collaboration between many types of scientists: biologists, geologists and chemists of various kinds.

To the critics I would quote from Faust:

Es irrt der Mensch so lang er strebt* (The Lord; Faust, Prologue in Heaven) Wer immer strebend sich bemüht den können wir erlösen† (Angel Choir, Ibid, II: 5)

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^{*} As long as man is striving he is in error

[†] We can redeem whoever continues to strive

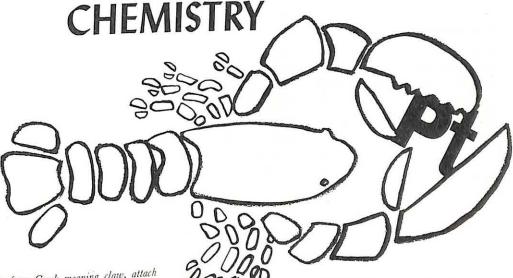
A SUMMER SHORT COURSE IN COORDINATION

hemical compounds can be thought of as combinations of different elements involving varying degrees of electron sharing. One extreme, the ionic bond, involves almost complete transfer of charge, as in the formation of Na+Cl- from Na and Cl atoms. On the other hand, covalent bonding represents a more or less equal sharing of negative charge, as in carbon tetrachloride, CCl₄:

CI CI:C:CI CI

Both carbon tetrachloride and sodium chloride differ radically in physical and chemical properties from their elemental constituents and both are stable chemical entities.

Complex compounds, on the other hand, may be considered as molecular or addition products



Chelates, from Greek meaning claw, attach themselves in a clawlike fashion to a central metal atom

Part I: Bonding Theories

Gert G. Schlessinger Gannon College, Erie, Pa. resulting from the combination of compounds such as those described above to form new materials which likewise differ from the parent substances. The distinction, then, between so-called simple and complex compounds is that simple compounds use elements as building blocks, but complex compounds use preformed compounds.

The transition elements of importance to our discussion fall in Groups VIB, VIIB, VIIIB, IB, and IIB of the periodic table; that is, chromium through zinc, molybdenum through cadmium, and tungsten through mercury. They owe their unusual properties to unfilled inner electron shells or, more specifically, the *d* orbitals.

Complex compounds, of which numerous examples are known, may be divided into two

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broad classes—normal complexes and penetration complexes. Normal complexes are those which dissociate reversibly in solution. For example,

$$(NH_4)_2CrCl_5 \cdot H_2O$$
 or $2NH_4Cl \cdot CrCl_3 \cdot H_2O$
 $(NH_4)_2CrCl_5 \rightleftharpoons 2NH_4^+ + Cr^{+3} + 5Cl^-$
and $Co(NH_3)_6Cl_2$ or $CoCl_2 \cdot 6NH_3$
 $Co(NH_3)_6Cl_2 \rightleftharpoons Co^{+2} + 2Cl^- + 6NH_3$

These are double salts because, when dissolved in an appropriate solvent, they show the combined chemical and physical characteristics of

each component, ion, or molecule.

and

Penetration complexes are those compounds which, when in solution, exist as ionic aggregates of greater stability than the double salts. For example,

$$K_4Fe(CN)_6$$
 or $4KCN \cdot Fe(CN)_2$
 $K_4Fe(CN)_6 \rightarrow 4K^+ + [Fe(CN)_6]^{-4}$
 $Rh(NH_3)_6Cl_3$ or $RhCl_3 \cdot 6NH_3$
 $Rh(NH_3)_6Cl_3 \rightarrow [Rh(NH_3)_6]^{+3} + 3Cl^{-4}$

The difference between the two classes of complexes is essentially a matter of degree. Both are formed by interaction of a metal (as its salt), called the central atom or ion, with various anions or molecules, called ligands, containing an unshared pair of electrons.

The ligands are attached to the central ion by so-called dative, coordinate covalent, or semi-polar bonds using their lone electrons. For example,

$$\begin{bmatrix} H_3N: & :NH_3 \\ H_3N: \rightarrow Pt \leftarrow :NH_3 \\ H_3N: & :NH_3 \end{bmatrix}^{+4} + CI^{-1}$$

The metal plus ligands that surround it comprise the coordination sphere which is shown by the square brackets.

Because of limited space, only penetration complexes or coordination compounds of the elements listed above will be considered.

History of the Theory

The historical development of experimental and theoretical progress in coordination chemistry can be divided into three major periods: the late eighteenth century to 1893; the Wernerian era, 1893 to 1940; and the modern period, 1940 to the present.

Because coordination compounds occur in nature, particularly in dyes and pigments, we can assume that they were used by the ancients, although the ancients had no knowledge of their true nature. For example, alizarin, a red dye prepared from madder root and clay, was used [Sutton, L., J. Chem. Ed. 37, 220 (1960)].

Coordination chemistry probably originated in 1704 with the discovery of the pigment Prussian blue by a Berlin color maker, Diesbach. Its preparation, which would make a present-day chemist wince, went like this: Equal parts of potassium nitrate, potassium antimonyl(III) tartrate (cream of tartar), and either ox blood or animal flesh were heated together. The product was dissolved in water, treated with ferrous sulfate, alum (potassium aluminum sulfate), and finally with hydrochloric acid. Today, we simply mix a ferric salt with potassium hexacyanoferrate(II) to obtain the pigment:

Fe⁺³ + K₄[Fe(CN)₆] +
$$x$$
H₂O \rightarrow
KFe^{III}[Fe^{II}(CN)₆] $\cdot x$ H₂O + 3K⁺

In 1753 Macquer prepared potassium hexacyanoferrate(II) by treating Prussian blue with alkali. About 1760 Lewis reported the use of potassium hexachloroplatinate(IV) (K₄PtCl₆) in refining platinum.

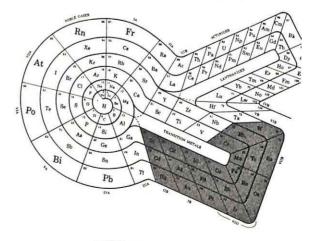
In 1799, Tassaert obtained orange CoCl₃-6NH₃ by allowing a mixture of cobalt(II) chloride and aqueous ammonia to stand in air:

$$4\text{CoCl}_2 + 24\text{NH}_3 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow$$

$$4[\text{Co(NH}_3)_6]^{+3} + 8\text{Cl}^- + 4\text{OH}^-$$

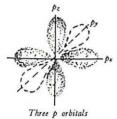
The puzzled French chemist recognized that a new chemical substance was formed, by combination of two stable or fully saturated compounds, which had very different properties from either.

During the next 50 years some activity was centered on other complex cobalt, iron, and platinum compounds, notably the preparation

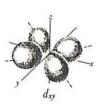


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of potassium hexacyanoferrate(III) [K₃Fe-(CN)₆] in 1822, tetrammineplatinum(II)tetrachloroplatinate(II) [Pt(NH₃)₄PtCl₄] by Magnus in 1828, and sodium nitrosylpentacyanoferrate-(III) [sodium nitroprusside, Na₂(Fe[CN]₅NO)] in 1849.

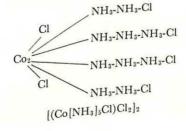
Beginning with Genth's work on the composition of the cobalt(III) ammines in 1847 we enter a fruitful period of empirical work by Fremy, Blomstrand, Gibbs, and particularly Jorgensen in Copenhagen which lasted until 1890. About 1851 Fremy devised color-code names for the cobalt ammines. In 1854 Claus recognized the submergence of the normal properties of ammonia (and water) molecules in these compounds but his ideas were not accepted then because sufficient experimental evidence was lacking.

In 1858 and 1865, two events occurred which were to hold back the development of coordination chemistry for almost 50 years. The first was Kekulé's theory of the tetrahedral and chain-like nature of carbon atoms. The second was emergence of the classical hexagonal formula of benzene. The rapid acceptance and verification of these valence principles in organic chemistry caused chemists working with penetration complexes to propose all sorts of unwieldy chain structures for their compounds; this originated with Blomstrand in 1871.

From 1870 to 1890 Jorgensen was the recognized master of the field. He prepared and carefully characterized large numbers of complexes but used and extended Blomstrand's chain formulations. His painstaking work and meticulous observations laid the groundwork for Werner's theory. Typical of some of these earlier formulas were:

$$\begin{array}{c} NH_{3}-NH_{3}-NH_{3}-Cl\\ \\ NH_{3}-NH_{3}-NH_{3}-Cl\\ \\ [Co(NH_{3})_{6}]Cl_{2} \end{array}$$

 $\begin{array}{c} \text{Cl-H}_3\text{N--Co--NH}_3\text{--NH}_3$



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The work of Raoult and van't Hoff on the properties of nonvolatile compounds in solution about 1882 allowed the determination of molecular weights and discarded dimeric (doubled) formulas such as those above. Also, in 1887, when Arrhenius introduced his concept of ionization, the difference between coordinated molecules (or ions) and fully ionized groups was clarified.

Werner's Theory. The stage was thus set in 1891 for Alfred Werner, then only 25 years old, to publish his first epoch-making paper on valence. In it he suggested that the central atom or ion does not necessarily have a small fixed number of valence bonds but that its valence might be exerted over the whole surface of the metal atom and have units of different affinity or strength.

Two years later, Werner, then assistant professor at Zurich, had considered the problem further and was led to think about molecular compounds in general. It is said that the answer came to him in a dream [Sutton, L., J. Chem. Ed. 37, 220 (1960)]. He awoke at two o'clock one morning with the entire problem solved in his mind and went into a room with pen, paper, and a box of cigars. He wrote until five the following afternoon to complete his theory [Werner, A., Z. Anorg. Chem. 3, 267-330 (1893)]. As a result, he was promoted to a full professorship that year and won the Nobel prize in 1913. Over the period 1893 to 1919 a prodigious amount of work came out of his laboratory, all of which has substantiated his postulates and served as the foundation of coordination chemistry ever since.

The fundamental principles of Werner's theory can be summarized as follows:

- 1. Metals possess two types of valence: Primary or ionic and secondary or nonionic (coordinate covalent bond type).
- 2. Every metal has a fixed number of secondary valences, either four or six (other numbers such as two, five, seven, and eight are recognized today).
- 3. Primary valences are satisfied by anions, while secondary valences may be filled with anions or neutral molecules. In every case the coordination number (C.N.) of the metal must be completed.
- 4. The secondary valences are directed spatially around the central metal ion. A C. N. of four requires a tetrahedral or planar configuration, while a C.N. of six is directed to the apices of a regular octahedron. These geometries predicted a variety of types of isomerism in penetration complexes; this postulate was the most difficult to prove. It was not until 1914 that Werner finally achieved the resolution of a purely inorganic compound.

In the so-called modern period of coordination chemistry, perhaps the major area of concern has been the gradual elucidation of bonding in penetration complexes [Sutton, L., *J. Chem. Ed.* 37, 498 (1960)].

In 1916 G. N. Lewis advanced his ideas on electronic bonding which involved the now elementary octet structure as applied to the valences of all atoms in compounds. For an atom or ion to have all its valence potential satisfied, the outer shell of electrons had to contain eight electrons. For example, for NH₃, the three H's each contribute one electron:

This principle, which worked well for most simple substances, was extended in the years 1923 to 1927 by Sidgwick and Lowry to coordination complexes. For example, the Co+3 ion has 24 electrons and can accept (by semipolar bonding) 12 more from six coordinating groups, each with a pair, to achieve maximum stabilitythat is, the inert gas configuration of krypton with 36 electrons. This effective atomic number (EAN) was arrived at by taking the atomic number of the element, subtracting the electrons lost in ion formation, and adding the electrons contributed by coordination. However, many relatively stable penetration complexes gave EAN's which were not those of a noble gas. For example, in CrCl3·6NH3, Cr has 24 effective electrons; Cr^{+3} , 21; and $6NH_3$, 6×2 , 12. This gives a total EAN of 33. Furthermore, this theory was unable to account for the spatial arrangement of ligands around the central metal.

Valence-Bond Theory. The next major step was due to Linus Pauling who, in 1931, introduced the valence-bond theory which contained three important new ideas. The first was concerned with the geometry of complexes with different C.N.'s, explained by the so-called hybridization of electronic orbitals. These orbitals are electron density patterns around the positive nucleus, and each can contain a certain number of electrons. The s orbitals can contain up to two electrons with opposite spins. The p orbitals have a maximum of six electrons, two in each p orbital. The d orbitals can contain up to 10 electrons, two in each d orbital.

Thus, a combination of one s orbital with three p orbitals resulted in four sp^3 hybridized orbitals directed to the corners of a tetrahedron. Similarly, dsp^2 hybridization gave a square planar arrangement and d^2sp^3 combination gave a

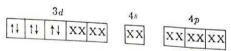
Table I. Electronic Distribution of Some Transition Metal Ions

rbitals			3d			48	4p
Cr	1	1	1				
+3 Mn ions Fe	†	1	†	1			
	1	1	1	1	1		
	11	1	t	1	1		
Ni +2 ions Cu Zn	†↓	11	11	1	1		
	11	11	†↓	11	1		
	11	11	†↓	†↓	↑↓		

regular octahedral orientation. All these hybrid orbitals were stronger than the simple orbitals alone and all orbitals of a hybridized set have the same energy.

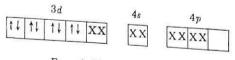
Because in Table I the energy differences of the 3d, 4s, and 4p orbitals are relatively small, the empty s and p orbitals may reasonably be involved in hybridization.

The formation of octahedral $Co(NH_3)_6^{+3}$ was explained diagrammatically as



Six d^2sp^3 hybrid orbitals

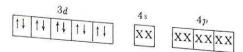
where X's represent electrons from the nitrogen atoms of the six ammonia molecules. Square planar $\mathrm{Ni}(\mathrm{NH_3})_4^{+2}$ may be represented diagrammatically as



Four dsp2 hybrid orbitals

Note that the two unpaired electrons of Ni⁺² have combined in one 3d orbital to form the complex ion. This will be explained under magnetic properties below.

Tetrahedral Zn(NH3)4+2 would contain



Four sp3 hybrid orbitals

The second principle of Pauling's valencebond theory concerned the magnetic properties





Shape of Metal Compleses



Octahedral



Tetrahedral



of many complex salts which might be used to investigate the nature of bonding between the ligand and central ion. If the coordination sphere has one or more unpaired electrons alone in an orbital, the compound will be attracted into a magnetic field and is said to be paramagnetic. With no unshared electrons, the complex will be diamagnetic or repelled by the field.

The movement of an electrical charge produces a magnetic effect, and if we think of an electron as a very small bar magnet, the magnetic moment is given by the strength of the poles multiplied by the distance between them. Polarity is set up in molecules due to variation in electron spin and cloud-charge distribution of the bonding orbitals between elements.

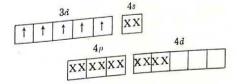
The total magnetic moment of a substance may be regarded as the result of all the moments of the individual electrons. It can be measured with a Gouy balance which weighs the substance in a strong uniform magnetic field of known strength and compares this weight to the weight of the substance when it is free of the field.

The magnetic moment thus measured is easily related to the number of unpaired electrons by the approximate relationship: Number of unshared $e^2s = X - (0.7 \text{ to } 0.9)$, where X = magnetic moment in Bohr magnetons (BM). The BM has the value of 5564 gauss cm. $^{-1}$ mole $^{-1}$ and is given by

where h is Planck's constant, 6.63×10^{-27} erg—second; ϵ is electron charge, 1.60×10^{-19} absolute coulomb; m is mass of electron, 9.11×10^{-28} gram; and ϵ is the speed of light in a vacuum, 3×10^{10} cm. per second.

The magnetic criterion is valueless for transition metals with fewer than four or more than seven d electrons. Thus Cr^{+3} complexes always show three free electrons and Cu^{+2} coordination compounds always show one.

The usefulness of Pauling's approach can be shown by a simple example. For [FeF₆]⁻³:



Six d^2sp^3 hybrid orbitals

Here there are five unpaired electrons, and we obtain a so-called outer orbital, ionic, or labile complex, in which outer 4d orbitals are used.

For [Fe(CN)₆]⁻³, the following applies:

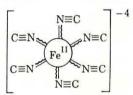
Six d²sp³ hybrid orbitals

where there is one unpaired electron and an inner-orbital type, covalent or penetration complex, using the inner 3d orbitals.

Note that in the last example, as in the case of the above-mentioned ammonia ion, trivalent iron pairs its previously lone electrons in complex formation. Pauling offered no satisfactory quantitative explanation of the differing effect of various ligands on the central ion's bond nature.

The third principle of Pauling's valence-bond theory concerned a type of double bonding between metal and ligands or a reverse electron donation of a partial nature which could spread out the negative charge over the whole coordination sphere. This would result in a more stable structure.

The coordination of various groups with their extra electrons might build up the minus charge on the central metal according to Sidgwick's theory. For example in $Fe(CN)_6$ ⁻⁴,



the iron(II) might have up to four excess negative charges. The metal could relieve itself of this electronic burden by partly "feeding back" some of these charges to the N≡C groups.

The valence-bond theory, for all its utility, was unable to provide quantitative explanations of bond strength and color in complexes. It also led to erroneous conclusions about ionic and covalent structure assignments based on magnetic data.

Electrostatic-Field Theory. From 1929 to 1935, the physicists Bethe and Van Vleck developed the crystal field theory for use in ionic crystal-lattice phenomena. Finally in 1951 and 1952, it was applied to coordination compounds by the German chemist Hartmann and the Englishman Orgel as the ligand or electrostatic field theory. It consists of the following simple postulates:

1. The central metal and ligands are hard



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spherical ions of opposite charge with the metal as positive. When the ligand is formally neutral, unshared electrons on the constituent atoms are regarded as local charged sites.

- 2. In the stable structure of the complex the particles are so arranged that oppositely charged species are in contact and like charges are separated as widely as possible.
- 3. The coordination sphere is energetically stabilized by the difference between all electrostatic attractions and repulsions of ions and molecules involved, and by the electrical interaction between the *d* orbitals of the transition metal and the electronic field of the ligands.

To begin with, consider an octahedral arrangement with six ligands approaching the central ion along opposite ends of the x, y, and z axes (see margin, page 12). The ligands will be repulsed most strongly by the $d_{z^2-y^2}$ and d_z : orbitals of the metal and least strongly by the d_{xy} , and d_{yz} orbitals because of their geometric orientation (see orbital diagrams, page 10).

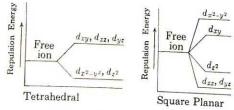
Free ion

All orbitals of equal energy (or degenerate)

Low energy (low repulsion) orbitals

High energy (high repulsion) orbitals d_{xy}, d_{xz}, d_{yz}

Similar spatial considerations for tetrahedral and square planar complexes are illustrated in the following diagrams:



An approaching ligand with a strong tendency to donate its electrons—for example, NH₃ or CN—results in a strong field environment and a pairing up of the central ion's electrons (which were previously unpaired in the *d* orbitals) due to the repulsions set up. Thus, a low spin or spin-paired penetration complex is formed of the inner-orbital or covalent type.

A weakly electron-donating ligand produces a weak field and gives a high spin or spin-free relatively unstable complex with outer-orbital or ionic features. If we use the Hund rule which states that electrons will occupy separate degenerate orbitals, then the electronic distribution of the *d* orbitals for the transition metals can be summarized in Table II.

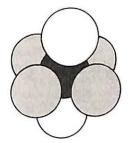
 Table II.
 Electronic Distribution of the d Orbitals for Transition Metal Complexes

		Н	igh S	Spin	Oatab	Low Spin Octahedral					
	d_{xy}	d_{xz}	dyż	d ₂ 2	$d_{x^2-y^2}$		dxz	d_{yz}	d_{z^2}	$d_{x^2-y^2}$	
d3 Cr+3	1	1	1	100		T t	1	1	T		
d4 Mn+3	1	1	1	†	etra c	11	1	t.	F		
d ⁵ Fe ⁺³	1	†	1	1	1	†↓	↑↓	1			
d6 Co+3	11	1	1	†	1	†↓	†↓	† 	-		
d7 Co+2	11	†‡	1	1	1	†↓	†↓	† ‡	1		
d ⁸ Ni ⁺²	11	†↓	11	†	1	1+	† ‡	1+	†	†	
d ⁹ Cu ⁺²	†↓	11	†↓	†↓	1	↑↓	†↓		-		
d10 Zn+2	11	11	11	†↓	11	1+	1+	† †	† 		
V-2-101		1	1	. 11			-	1.4	11+	1+	
			11111		Tetrah	edral	17				
d^3	1			1	1				11	1	
d4	1	1	10	1	1				11	†↓	
d5	1	1	†	1	1	1			11	† 	
d ⁶	1	1	1	11	1	1	†		†↓	† ‡	
d ⁷	1	1	1	†↓	†↓	1	1	1	↑↓	† +	
d ⁸	11	1	1	11	11	† 	1	1	↑↓	†↓	
d 9	11	11	1	11	11	11	1+	+	1+		
d10	11	11	1	11	11	†↓	† ţ	†↓	11	<u>↑</u> ↓	
					to said	The state of	100		Plana		
					d ⁷	1	†↓	11	11		
					d ⁸	11	11	†↓	†↓		
THE ST					d 9	11	† ‡	†↓	†↓	1	

Only the configurations d⁴ through d⁷ differ in high and low spin complexes and the electronic assignments are similar to Pauling's except with the modification of differing orbital energy levels. However, this last distinction gives the ligand field theory its most useful quantitative aspect in its ability more simply and accurately to evaluate bond strengths, kinetics, and color in all types of complexes without recourse to often misleading magnetic data.

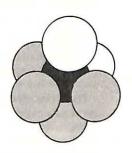
Much remains to be done before an all-encompassing coordination theory will evolve; it seems increasingly likely that no simple one will suffice. Nevertheless, the close historical parallel between complex and general chemical bonding theory is interesting. Experimentation and technology must reach a certain stage before a new idea is ripe for general acceptance.

For a more detailed discussion of ligand field theory see Chemistry, January 1966, page 14.



Part II: Nomenclature and Physical Properties

Geometric isomers of dichlorotetramminecobalt(III), [Co(NH3)4Cl2]+. Trans on left, green; eis on right, violet



A SUMMER SHORT COURSE IN COORDINATION CHEMISTRY

GERT G. SCHLESSINGER, Gannon College, Erie, Pa.

In 1852, Fremy suggested color-code names for cobalt complexes. Later these were frequently used as generic-type prefixes for other metals with similar formulas but with different colors (Table III). These names are still encountered in the older literature, but they have been replaced by a more systematic method of nomenclature.

Current Nomenclature

The current system of nomenclature, a modification of Werner's rules, involves these steps: The cation is named first. Then the coordination sphere is specified as follows: Bonded groups are listed with negative groups first, then neutral groups, and positive groups last. Negative groups end in -o; neutral groups normally have no suffix, except aquo (water); and positive groups end in -ium. Among neutral groups aquo is listed first; ammine (ammonia) last. The number of each simple ligand is prefixed to the name; for example, di-, tri-, tetra-, penta-, and hexa-. For complicated ligand names, bis-, tris-, tetrakis-, pentakis-, and hexakis- are used. The name of the metal is given, with a Roman numeral in parentheses as suffix to indicate the oxidation state. If the coordination sphere is negative, the metal name ends in -ate and the Roman numeral follows.

Some representative examples of current nomenclature are: $K[Co(NH_3)_2(C_2O_4)(NO_2)_2]$, dinitrooxalatodiamminecobaltate- $(III)\,;\quad [\mathrm{Co}(\mathrm{NH_3})_3(\mathrm{H_2O})\mathrm{Cl_2}]\mathrm{HSO_4},\quad dichloro$ aquotriamminecobalt(III) hydrogen sulfate; [Co(NH₃)₆][Cr(CN)₆], hexamminecobalt(III) hexacyanochromate(III); [Ni(NH₃)₄(NO₂)₂],

dinitrotetramminenickel(II); and H[Co(NH₃)₂-(C2O4)2], hydrogen dioxalatodiamminecobaltate(III).

Typical Ligands

Table IV lists some of the more important ligands. A ligand which occupies more than one position in the coordination sphere is referred to as bi-, tri-, tetra-, penta-, or hexadentate. These polydentate ligands are known as chelates (from the Greek chele, crab's claw). An example of a bidentate ligand is ethylenediamine, H2N-CH2-CH2-NH2, which can attach itself to a metal ion by the unshared electron pairs on both nitrogen atoms.

Stereoisomerism

Werner suggested three basic spatial geometrical arrangements for complexes: octahedral, tetrahedral, and square planar. To

Table III. Early Nomenclature

Generic				
Туре	Name	Color		
$[Co(NH_3)_6]^{+3}$	Luteo	Yellow		
[Ir(NH ₃) ₆] ⁺³	Luteo	Colorless		
[Co(NH ₃) ₅ Cl] ⁺²	Purpureo	Purple red		
[Ir(NH ₃) ₅ Cl] ⁺²	Purpureo	Pale yellow		
[Co(NH ₃) ₅ I] ⁺²	Purpureo	Olive green		
[Co(NH ₃) ₅ H ₂ O] ⁺³	Roseo	Rose red		
[Ir(NH ₃) ₅ H ₂ O] ⁺³	Roseo	Colorless		
cis-[Co(NH ₃) ₄ (NO ₂) ₂]+	Flavo	Brown yellow		
trans-[Co(NH ₃) ₄ (NO ₂) ₂]+	Croceo	Crocus yellow		
cis-[Co(NH ₃) ₄ Cl ₂] ⁺	Violeo	Violet		
trans-[Co(NH ₃) ₄ Cl ₂] ⁺	Praeseo	Green		

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Octahedral



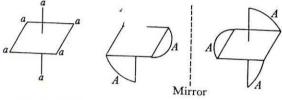
Tetrahedral



Square planar

simplify the discussion, unidentate ligands are labeled a, b, c, and so forth, and bidentate ligands, A, B, C, and so forth. The three basic coordination sphere shapes can be projected diagrammatically as shown at the left. The metal atom is in the center of each. Note that each position is equivalent to any other.

The Octahedral Model. Ma6 can have only one configuration, but MA3 can have two arrangements which are mirror images of each other and nonsuperimposable. Such a pair of isomers is known as a pair of optical isomers or enantiomorphs because one of the few distinguishing features between members of the pair is their ability to rotate polarized light in equal and opposite directions. The twin which is rightturning is called dextrorotatory or the d form, while the left-turning twin is the levorotatory or l form. The together are sometimes referred to as a pair. An example of Ma6



is $[Co(CN)_6]^{-3}$ and of MA_3 is $[Co(en)_3]^{+3}$, where en is ethylenediamine, H2N-CH2-CH2-NH2.

Note that the total charge on the complex

Table IV. Some Important Ligands

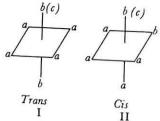
Position of Key Atom in Periodic Table	Unidentate	Bidentate	D.I. I
Group IVa	CO ₃ -2, CO	CO ₃ ⁻² , C ₂ O ₄ ⁻²	Polydentate
Group V ^b	NH ₃ , CN ⁻ , NO, NO ₂ ⁻ , NO ₃ ⁻ , Amines (RNH ₂), R ₃ P, R ₃ As, R ₃ Sb, R ₃ Bi	Organic 1,2- and 1,3- diamines; for example, H ₂ NCH ₂ CH ₂ NH ₂	Organic polyamines
Group VI°	SO ₄ -2, SCN-, S ₂ O ₃ -2, SeCN-, TeCN-, H ₂ O, OH-	SO ₄ ⁻² , SO ₃ ⁻² , S ₂ O ₃ ⁻²	
Group VII	F-, Cl-, Br-, I-		

R = organic group. Ligands include all types of olefins), acetylenes (—C≡C—), aromatic hydrocarbons, and cyclopropane, as well as isonitriles (RCN). b Ligands include all types of aromatic nitrogen molecules; for example,

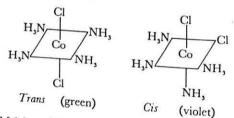
Ligands include many organic molecules containing oxygen, such as alcohols

and phenols (ROH), ethers (ROR), acids (RCO₂H), and oximes (R₂=NOH using N and O atoms).

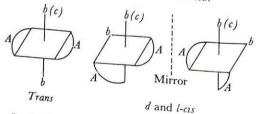
ion is the sum of all the constituent ions because neutral ligands do not contribute to any change in overall charge. Ma_5b has no isomers. Ma_4b_2 and Ma_4bc have two isomers.



Structures I and II are so-called geometric isomers which have the same formula but simply differ in the arrangement of ligands around the metal. Geometric isomers differ in both physical and chemical properties in contrast to mirrorimage pairs. If the ligands b are grouped next to each other, the name of the complex is prefaced by cis. When the two groups are at opposite ends of the octahedron, the prefix trans is used. Thus, Ma4b2 has a pair of cis-trans geometric isomers. An example is the ion [Co(NH₃)₄Cl₂]+. The trans form is green and the cis form is violet.



 $\mathrm{M}A_2b_2$ and $\mathrm{M}A_2bc$ are the most interesting cases for our purpose. There are three isomers:

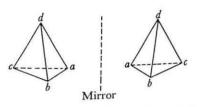


In this instance, the cis form exists as a dl pair. The ion [Cr(en)2Cl2]+ falls into this category and has similar colors to the dichlorotetrammine complex discussed previously. Three isomers are known, of which two are mirror-

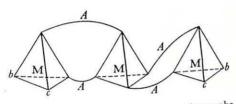
Whenever a cis complex is produced in the laboratory, an optically inactive blend of exactly equal parts of d and l mirror images is formed which is known as a racemic mixture or racemate. These racemates can be separated or resolved by special techniques which make use of the lack of symmetry of the structures.

Further treatment of the hexacoordinate octahedral type is left to the ingenuity of the reader. The magnitude of the problem becomes staggering if one considers a compound of type (Mabcdef), for which 15 pairs of enantiomorphs are predicted theoretically. As a test of your skill and understanding of the problem, work out the number of stereoisomers for the following octahedral complexes and indicate which of them exist as dl pairs: Ma3b2c; Ma3bcd; Ma2bcde; MAb2c2; MAb2cd; and MAbcde. The answers are given on page 32.

The Tetrahedral Model. The only case of isomerism in carbon compounds is Mabed

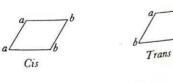


where a dl pair is predicted. This is true, however, only in cases where one central atom is involved in coordination. A trinuclear tetrahedral complex, type $M_3A_4b_2c_2$, with structure



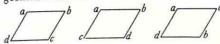
would be expected to exist as two enantiomorphs. Note that this is also true for M3A4b2cd and M3A4bcde, provided the end groups stay attached to a given metal atom. If, however, the various ligands can be interchanged, the number of isomers increases to two dl pairs for the first case and three pairs for the second. See if you can work out these examples on paper or, better, with models.

The Square Planar Model. Mas, Masb, MAb_2 , MA_2 , or MAbc exist in only one form. They have no isomers. A compound of form Ma2b2 can exist as a cis-trans pair:



In this cis case, however, no enantiomorphic forms are possible. An example of this kind is Pt(NH3)2Cl2. Both isomers are yellow, but the cis form is somewhat deeper colored than the trans isomer. Ma2bc also has a pair of geometric cis-trans forms as above; for example, [Pt(NH3)2-(SO₄)(H₂O)].

Finally, the type Mabed should have three geometric isomers:



The synthesis of these three isomers has been realized in the case of [Pt(NH3)(NO2)(C5H5N)-(H2NOH)]+ and none of the isomers prepared could be resolved into a mirror-image pair.

The three spatial arrangements of inorganic complexes propounded by Werner in analogy pair of to organic compounds have been verified in many cases. However, many predictions of his stereochemical theory have not, as yet, been murror-image pair demonstrated in the laboratory. It is, nevertheless, significant that no evidence contradictory to Werner's coordination postulates has yet come to light. The problem then is one of incompleteness rather than of errors of assumption. The theory is retained, therefore, until it can be systematically disproved.

Other Kinds of Isomerism in Complexes

Coordination Isomerism. This phenomenon arises when a set of given ligands is distributed around different central metals. For example, [Cu(NH₃)₄][PtCl₄] and [Pt(NH₃)₄][CuCl₄] are coordination isomers. So are [Co(NH3)6][Cr-(SCN)₆] and [Co(NH₂)₄(SCN)₂][Cr(NH₃)₂-(SCN)4]. These isomer pairs have properties differing completely from one another.

Polymerization Isomerism. This term applies to a series of totally different complexes which are multiples of a basic unit compound. Some examples are shown below.

No. of Units	Formula
1	[Co(NH ₃) ₃ (NO ₂) ₃]
2	$ \begin{array}{c} [\text{Co(NH_3)_6}]^{+3} [\text{Co(NO}_2)_6]^{-3} \\ \text{and } [\text{Co(NH_3)_4(NO}_2)_2]^+ \ [\text{Co(NH_3)_2(NO}_2)_4]^- \end{array} $
3	[Co(NH ₃) ₅ NO ₂] ⁺² 2[Co(NH ₃) ₂ (NO ₂) ₄] ⁻
4	3[Co(NH ₃) ₄ (NO ₂) ₂] ⁺ [Co(NO ₂) ₆] ⁻³
	3[Co(NH ₃) ₅ NO ₂] ⁺² 2[Co(NO ₂) ₆] ⁻³

Ionization Isomerism. When two different complexes have the same composition but have

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Table V. Electrical Conductivity of 1 Mole of Complex Compounds in 1000 Liters of Water at 25° C.

Ions Present No.	Example	Conductance Range, Ohms	
2	K+, [Co(NH ₃) ₂ (NO ₂) ₄]- similar to NaCl	95-120	
3	[Co(NH ₃) ₆ Cl] ⁺² , 2Cl ⁻ Similar to BaCl ₂	225-280	
4	[Co(NH ₃) ₆] ⁺³ , 3Cl ⁻ Similar to AlCl ₃	380-435	
5	4K+, [Fe(CN) ₆]-4	520-560	

their ligands arranged differently in the coordination sphere, they are called ionization isomers. For example,

[Co(NH3)4(H20)c]]+

$$\begin{array}{c} [\mathrm{Co(NH_3)_4(NO_2)(SCN)}\,]^+\mathrm{Cl}^- \\ \mathrm{VI} \end{array}$$

Structure IV yields only ionic thiocyanate in solution, while the chloride and nitrite anions are bound as coordinated species and do not give characteristic qualitative tests. Similarly, structure V yields only nitrite, and structure VI, chloride.

If this isomerism is brought about by a difference in coordinated vs. crystal lattice water molecules (water of crystallization), the specific

Table VI. Some Compounds Exhibiting Unusual Valence States for Metals in the First Transition Series

Metal	Com- mon Va- lence		Oxidation State	Series	
Cr		0	1	3	
Ci	2, 3	$Cr(CO)_6$ $Cr(RNC)_6$ $Cr(C_6H_6)_2$	(C ₆ H ₆)CrI	3	
Mn	2	Mn ₂ (CO) ₁₀	70.10		
P			K ₅ Mn(CN) ₆ CH ₂ Mn(CO) ₅	K ₃ Mn(C ₂ O ₄);	
Fe	2, 3	Fe(CO) ₅ Fe ₂ (CO) ₉ Fe ₃ (CO) ₁₂ (RNC) ₂ Fe(CO) ₃ (RNC) ₂ Fe(NO) ₂	Fe(NO) ₂ I		
Со	2	$Co_2(CO)_8$ $(C_2H_2)_2Co_2(CO)_6$	CH ₃ Co(CO) ₄ (RNC) ₅ CoI		
Ni		K ₄ Ni(CN) ₄ Ni(CO) ₄ Ni(PCl ₃) ₄	Ni(NO)I K ₂ Ni(CN) ₃ (NO) K ₄ Ni ₂ (CN) ₆		

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phrase, hydrate isomerism, is used. For example, $[Co(NH_3)_3(H_2O)_2Cl]Br_2$ and $[Co(NH_3)_3(H_2O)-ClBr]Br\cdot H_2O$. The first material has all and the second only half its bromine in the ionic form. Ionization and hydrate isomers differ in physical and chemical properties.

Conductance of Penetration Complexes

A readily applicable and widely used method of studying coordination compounds is the measurement of electrical conductivity in water. This approach depends on the fact that coordinated ions, for example Cl⁻ in FeCl₆⁻³, do not carry current in solutions; thus, the proper assignment of complexed and ionic ligands can be determined. If we choose solutions containing 1 mole of the salt in 1000 liters of water at 25° C., we obtain values in reciprocal ohms, as shown in Table V.

For example, the conductivity of CoCl₃-4NH₃·H₂O indicates the presence of three ions. This, taken together with the facts that the ammonia molecules are complexed and the coordination number of Co⁺³ is six, leads to the formulation of the substance as [Co(NH₃)₄-(H₂O)Cl]Cl₂. This is further substantiated by the observation that only two thirds of the total chlorine present can be precipitated as AgCl with cold silver nitrate.

An important corollary of Werner's ionization theory is that materials such as $[Co(NH_3)_3-(NO_2)_3]$ or $[Pt(NH_3)_2(SO_4)(H_2O)]$ should be nonelectrolytes or nonconductors in aqueous solution. This is verified by careful conductometric studies.

Other physical methods which are used to determine the number of ions a complex yields in solution, as well as the molecular weight, include freezing point depression, boiling point elevation, and osmotic pressure. These techniques, based on the so-called colligative properties, are treated in general and physical chemistry textbooks.

Oxidation States of the Transition Metals in Coordination Compounds

One of the many fascinating aspects of penetration complexes is their ability to stabilize lower valence states of transition metals which do not occur in simple salts. Table VI lists some known compounds exhibiting unusual valence states for metals in the first transition series. Numerous similar complexes are known of other transition elements and may be found in advanced textbooks.



PART III. APPLICATIONS

We live in a world of coordination compounds which contain the key to many life processes and scientific advances. Our increasing understanding of these vital compounds have led to many uses

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While the development of coordination chemistry has been of great significance in our understanding of chemical structure and bonding, relatively few complex compounds have found practical use in industry. However, a number have been used successfully for analytical separations based on differing stabilities of a mixture of metal ions toward a given ligand, usually of the chelate type. Also, certain complexes are fundamental to life processes in plants, fishes, and mammals.

Chemical Analysis

Organic chelating ligands often allow selective precipitation of certain metal cations in the presence of others which would normally interfere if inorganic cationic reagents were used (12). For example, nickel contaminants were separated from cobalt salts by preferential formation of [Co(NH₃)₃Cl]Cl₂; nickel gives no analogous compound but remains in solution after filtration of the pentammine salt. Now, however, dimethylglyoxime can be used to separate nickel and cobalt by precipitating nickel as the red, solid bis(dimethylglyoximato)nickel(II) while cobalt remains in solution.

Bis(dimethylglyoximato)nickel(II)

Note that in this complex one hydrogen has

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Table VIII. Some Organic Chelating Ligands and Their Analytical Uses

Reagent	Formula	Analytical Use	
Benzoinoxime	H ₅ C ₆ —H C—C ₆ H ₅	Cu, Mo, Ni	
Cupferron	H ₂ C ₆ —N \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	Fe, Ti, V, Sn, U, Ta, etc.	
Oxine (8-hydroxyquinoline)	HC N C C CH HC C C C CH HC C C C CH	Mg, Cu, Fe, Pd, Al, etc.	
Dithizone	$S=C \begin{cases} H & H \\ N-N-C_0H \\ N=N-C_0H_0 \end{cases}$	Cu, Pb, Zn, Co, Ni, Bi, Tl	
1-Nitroso-2-naphthol	НС ССССН НС ССССН НС ССССН	Co, Cu, Fe, Pd, Cr, Sn, Ag, V, U	
Dithiooxamide	HN=C-C=NH SH SH	Cu, Co, Ni, etc.	
Cyanides	CN -	Ni, Ag, Hg, Cu	
Thiocyanates	SCN -	Zn, Cd, Cu	

HON=CCH₃ HON=CCH₃ Dimethylglyopime been lost from each ligand as H^+ so that the material is actually a nonelectrolyte because nickel was originally in the +2 state.

Table VIII contains some important organic chelating ligands. For a more complete listing, analytical chemistry texts may be consulted (9).

Metal Production

Nickel was the first metal to be purified with a coordination complex. The purification was first carried out in the early 1890's by the Mond process in which the crude metal is heated at 100° C. in a stream of carbon monoxide and volatilized as Ni(CO)₄. This vaporized liquid is then heated to regenerate pure nickel and carbon monoxide.

Niobium and tantalum, important metals in plastic surgery and aerospace programs, are

separated by preferential hydrolysis of their fluoride complexes. The niobium precipitates while the tantalum stays in solution.

Ion exchange resins have been used to produce hafnium-free zirconium for nuclear reactors. These resins employ a solution of the metal mixture in the form of fluoro complexes.

The Group IB and IIB metals are often commercially purified by electrodeposition from solution as cyano complexes. Ammonia and various amines can also be used in a similar manner. Use of organic chelates offers interesting future possibilities for the electroplating industry.

Catalysis

Two extremely important commercial processes use coordination compounds. The first involves complex titanium-aluminum catalysts

CxHyOH alcohol

c=c Olefins

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to produce polyethylene of superior quality and at lower temperatures and pressures than previous methods. This is known as the Ziegler-Natta process after the German and Italian chemists who developed it. The second, the oxo reaction, utilizes dicobalt octacarbonyl [Co2-(CO)₈] and "water gas" (H₂ + CO) to make numerous alcohols from olefins. This synthesis, developed by the Germans in World War II to provide starting materials for their chemical industry, is much used everywhere today.

Industrial Chelating Agents

A hexadentate ligand of great commercial ethylenediaminetetraacetic value (EDTA):

The two starred nitrogens and four starred oxygens (in the tetraanionic form) can wrap themselves spirally around an octahedron.

While this chelate will form complexes with transition elements, its most spectacular practical success has been in the complexation of calcium and magnesium ions (CHEMISTRY, June 1966, page 29). It is used as a water softener, wine and liquid soap clarifier, antidote for lead poisoning, and nutrient (as the soluble iron complex) for citrus trees growing in iron deficient soils. The use of EDTA and citric acid as complexometric ion exchange eluting agents has led to the industrial availability of pound quantities of lanthanide (rare earth) chemicals which in former times were rare laboratory curiosities.

Metal Complexes of Biological Significance

In mammals, hemoglobin, a protein-linked, complex iron(II) chelate, serves as a reversible carrier of molecular oxygen to all cells of the organism. Closely related copper(II) and vanadium(IV) compounds serve similar functions in many invertebrates. Within the animal cell another Fe(II)-Fe(III) protein-based coordination compound of the hemoglobin family called cytochrome C acts as a catalyst for the utilization of oxygen in the basic cell metabolism or fundamental life process. Chlorophyll, a magnesium complex again related to hemoglobin, converts carbon dioxide and water to starches and sugars in the plant kingdom. Solar energy

provides the driving force for this all-important series of transformations.

It has been suggested that green plants, particularly algae, could serve not only as food but also to absorb CO2 and to release O2 for use by astronauts on long space flights. A complicated cobalt complex with the forbidding name of bis(disalicylalethylenediamine) - µ - aquodicobalt-(II) (Salcomine) has the remarkable property of reversibly taking up oxygen under slight pressure and releasing it under gentle warming. It is safer to use than liquid oxygen stored in tanks. Perhaps space engineers will find some use for it in interplanetary travel in the future.

Together with the insight we have gained into complexes, there will be corresponding technological advances. These will give man more effective control and better understanding of the world in which he lives, which is in large measure an environment of coordination compounds.

For Further Reading

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Chlorophylla

	100

8. Source book

8. Source de renseignements

WORLD VIEW

The American Chemical Society (ACS) sponsored an international conference on high school chemical education from 28 August to 2 September 1967, in Washington, D. C. The Proceedings of this conference, which was attended by some forty participants, have recently been published by the ACS under the title International Chemical Education: The High School Years. This section of New Trends summarizes some of the national programmes for development of chemical education which were reported in detail at the conference. The programmes of organizations such as Unesco and CREDO were also described and are summarized here. The appendixes to the conference papers contain much useful information on the chemistry syllabus in different countries, and these are reproduced here in full, together with a list of addresses of science education projects in various parts of the world.

EXAMINATIONS

This section reproduces the contribution made by J. Arthur Campbell on the topic of examinations in chemistry to the ACS conference, together with an appendix in which typical examination questions of different type from different countries are reproduced. The "multiple choice" type of examination is discussed in detail in an article by H. Kéri of the Budapest Technical High School for Chemistry.

VISUAL AIDS

The Advisory Council on College Chemistry in the United States has recently produced two useful and informative articles on visual aids: a report on the use of television and film in chemistry teaching and one on teacher-produced instructional films. Brief summaries of these reports are included here. The article by H. N. Alyea provides details and

L'ENSEIGNEMENT DE LA CHIMIE DANS LE MONDE

L'American Chemical Society (ACS) a patronné une conférence internationale sur l'enseignement de la chimie dans les écoles secondaires, qui a eu lieu, du 28 août au 2 septembre 1967. à Washington D. C. Les travaux de cette conférence, qui a groupé environ 40 participants, ont été publiés par l'ACS sous le titre International chemical education: The high school years. Cette section des Tendances nouvelles contient un résumé de certains programmes nationaux de développement de l'enseignement de la chimie, qui ont fait l'objet de communications détaillées à la conférence. Les programmes d'organisations telles que l'Unesco et le Centre for Curriculum Renewal and Educational Development Overseas (CREDO) ont également été décrits et s'y trouvent résumés. Les annexes aux documents de la conférence, qui contiennent de nombreux renseignements utiles sur les programmes de chimie dans divers pays, sont reproduites intégralement; on trouvera aussi une liste d'adresses relatives à des programmes d'enseignement des sciences dans diverses parties du monde.

EXAMENS

On trouvera dans cette section le texte de la communication présentée par J. Arthur Campbell à la conférence de l'ACS sur la question des examens de chimie, ainsi qu'une annexe contenant diverses questions d'examen types, provenant de différents pays. Le système d'examen à « choix multiple » est étudié en détail dans un article de H. Kéri, de l'école secondaire technique de chimie de Budapest.

AUXILIAIRES VISUELS

L'Advisory Council on College Chemistry des États-Unis a récemment publié deux articles très utiles et extrêmement instructifs sur les auxiliaires visuels: un rapport sur l'emploi de la télévision et du cinéma dans l'enseignement de la chimie et un autre sur la réalisation de films éducatifs par les enseignants. On trouvera ici de brefs résumés de ces rapports. diagrams for a wide variety of experiments devised for presentation by overhead projection.

PROGRAMMED LEARNING

The article by V. I. Levashev gives details of the way in which a course on "chemistry and agriculture" was taught by the programmed method using teaching machines. G. N. Seddon gives a critical review of some published programmes and discusses the fundamental principles of programme writing.

ABSTRACTS

The editor is grateful to the Esso Petroleum Company and to the General Editor for permission to reproduce the chemistry section of Science Teachers Abstracts 4. These abstracts refer to articles selected as being of particular interest to teachers of chemistry which appeared in 1967.

SCIENCE TEACHING JOURNALS

The list of journals concerned primarily with chemistry teaching which was compiled by Mrs. S. M. Haggis for Volume 1 of New Trends in Chemistry Teaching was one of the first of its kind to appear and many readers have indicated that they found it a useful feature. A revised and extended list has therefore been included here. The editor would be very grateful if editors and publishers would let him have details of any relevant publications which may have been inadvertently omitted.

ADDRESSES OF SCIENCE EDUCATION PROJECTS

This section consists of the addresses of various science education projects.

L'article de H. N. Alyea contient des explications et des schémas ayant trait à un grand nombre d'expériences destinées à être présentées par rétroprojection.

ENSEIGNEMENT PROGRAMMÉ

L'article de V. I. Levachev explique comment un cours de « chimie agricole » a été donné par la méthode d'enseignement programmé, au moyen de machines à enseigner. G. N. Seddon procède à l'examen critique de certains programmes publiés et étudie les principes fondamentaux de la rédaction des programmes.

COMPTES RENDUS D'ARTICLES SCIENTIFIQUES

Le directeur de la présente publication remercie l'Esso Petroleum Company et le rédacteur en chef de la revue qui lui ont permis de reproduire la section de chimie de Science teachers abstracts 4. Il s'agit de comptes rendus d'articles parus en 1967, qui ont été choisis en raison de l'intérêt particulier qu'ils présentent pour les professeurs de chimie.

PUBLICATIONS PÉRIODIQUES SUR L'ENSEIGNEMENT DE LA CHIMIE

La liste des revues portant essentiellement sur l'enseignement de la chimie qui avait été établie par Mme S. M. Haggis pour le volume I de Tendances nouvelles de l'enseignement de la chimie a été l'une des premières du genre à paraître, et de nombreux lecteurs ont fait savoir qu'ils l'avaient trouvée utile. C'est pourquoi on a fait figurer dans le présent volume une liste révisée et augmentée. Le directeur de la publication serait vivement reconnaissant aux directeurs de revues et éditeurs qui lui fourniraient des renseignements sur toute publication de ce genre qui pourrait avoir été omise par inadvertance dans cette liste.

On trouvera dans cette section les adresses de quelques proj^{ets} d'enseignement scientifique.

WORLD VIEW/L'ENSEIGNEMENT DE LA CHIMIE DANS LE MONDE

This section summarizes some of the contributions to the American Chemical Society conference on International Chemical Education: The High School Years held in Washington, D.C., from 28 August to 2 September, 1967.

Chemical Education Activities in Developing Countries
British Council and Credo by Dennis G. Chisman

The British Council was established to promote wider knowledge of Britain and of the English language overseas and to develop closer cultural and educational relations with other countries. Its greatest professional activity is in the field of education, especially the the teaching of the English language. A more recent and an increasing area of activity is the teaching of sciences and the Council assists science teaching overseas in a number of ways - e.g. providing full time Science Education Officers in West and East Africa, India and Pakistan, visits of selected reachers to Britain and short or long-term visits of specialists from Britain to assist with courses and advise on new curricula.

Centre for Curriculim Renewal and Educational Development Overseas (CREDO)
Was established in 1966 as a coordinating agency to respond to requests
from overseas for assistance with curriculum development projects. Its
efforts are being concentrated, initially, at the school level. Some
examples of CREDO's activities are as follows:
1. Africa

Nigeria: An attempt is being made to introduce a combined science course for the first two years in secondary schools. Nuffield schemes in chemistry, physics and biology are being rewritten and adapted to suit the country's needs.

West African Examinations Council. (WAEC): New syllabuses have been completed by teams of teachers and university lecturers working in Nigeria and Ghana. These chemistry syllabuses will be examined for the first time in 1968 or 1969. Courses are being planned to provide the help that teachers will need if the new syllabus is to be taught effectively.

East Africa: Trials of Nuffield Chemistry materials are under way in some 20 Tanzanian secondary schools and similar trials are likely to begin in Uganda, Kenya, Zambia, Lesotho, Botswana and Swaziland. New educational policy in Tanzania requires the development of curricula in Which the academic content is greatly reduced and the ways in which

chemistry is going to be relevant to the lives they are actually going to live is put in. There is, therefore, a strong agricultural bias.

2. India

Curriculum development is mainly the concern of the Lational Council for Educational Research and Training (NCERT) and the National Council for Science Education. Five study groups have been established to devise new curricula for high school chemistry. group is associated with a University and comprises university and school teachers. In addition there is a UNESCO-sponsored team in Delhi working full time on the preparation of texts and devising apparatus. CREDO has been invited to send British educators to spend some time with each of the study groups. A series of summer institutes for high school teachers has been held for a number of years, sponsored by U.S. AID, the University Grants Committee of India and NCERT. These institutes have been mainly concerned with the CHEM Study and CBA approaches. There is still considerable scope for radical changes in chemistry teaching in India.

3. Ceylon

The Ceylon Ministry of Education contributes considerable efforts to improving science and mathematics curricula in secondary schools. They are making available an increasing number of experienced teachers, inspectors and teacher trainers to work in a curriculum unit on devising and assessing new examination papers and preparing teachers

4. Pakistan

Educational extension and equipment contres have been established with assistance from the Ford Foundation and UNICEF is active in supplying science apparatus to schools and curriculum groups have been formed. The actual teaching in schools has not yet changed very

5. Malaysia

A science teaching centre is to be established in Penang which is expected to serve as a regional centre for S.E. Asia. CREDO has supplied some Nuffield texts and film loops for reference purposes, and will probably provide a comprehensive range of equipment for

In the discussion arising from this paper the importance of improving the standards of the teacher training colleges in the

Recent Developments in Chemical Education in Australia

by E.C. Watton

New Curricula A new six-year science curriculum has been introduced into secondary schools in new South Wales. The first part is an integrated treatment of biology, chemistry, geology and physics extending over the four-year period of the School Certificate Course. It is compulsory for all pupils but may be taken at three different levels according to ability. The second and final part is a two-year course (Higher Certificate) which is also provided at three levels but is not obligatory. A textbook and teachers' manual have been written. (ref.1)

The content of the Higher Certificate chemistry course at the highest level reflects that of its integrated science base and encompasses and extends beyond basic university matericulation requirements. The syllabus represents a considerable increase in depth of subject matter and is currently placing a heavier burden on the science teacher. Some widespread reaction to the senior syllabus has led to a considerable curtailment in content. Details of the syllabus will be found in (ref. 2).

New Texts In addition to the texts for the first four-year integrated course, a further work has been prepared under the aegis of the National Research Foundation. This is 'Senior Science for High Schools', which is in three separate volumes, one each for Schools', which is in three separate volumes, one each for biology, chemistry and physics. It is designed to support the longer biology, chemistry and physics. It is designed to support the longer of the second level syllabuses and to provide a guide for the extended of the second level syllabuses and to provide a guide for the extended of the first level syllabus (ref. 3).

Chemistry - a Structural View ' is another modern course of instruction designed by a group of university teachers and secondary school teachers in the state of Victoria. Intended for the final school teachers in the state of victoria is to be closely related to the year of the secondary school, it is to be closely related to the university entrance requirements of that state.

The 'Approach to Chemistry' series (ref.4) publishes the proceedings of the summer schools held annually in the School of Proceedings of the University of New South Wales. Associated with Chemistry of the University of New South Wales arranged this is a 'Chemical Data Book' containing selected data arranged this is a 'Chemical Data Book' secondary school and first in a manner considered useful for secondary school and first year university courses.

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Recent Developments in Chemical Education in Brazil by Isaias Raw

Chemistry in Brazil is taught at the Senior High School level (16 -18 years) for three years, in parallel with 3-year courses in Physics and biology. Chemistry instruction is preceded by four years of general science education. The basic purpose of secondary education is preparation for the university. Here there are two problems: (1) secondary schools were originally intended for a professional elite which did not want to soil its hands doing experiments, and (2) the number of candidates for university entrance grew more rapidly than the universities, which consequently have a limited enrollment. Entrance requirements are made more rigorous year by year. These requirements relate to written examinations which become totally incompatible with the aims of science education at the secondary level, not only as an education for the layman and the citizen, but even as an education for future university students planning to major in a science. Another problem is the uniform, federally controlled curriculum. This prevented innovation, and maintained a uniform and obsolete method of teaching for which different teachers wrote identical texts. Brazil is now free from this damaging arrangement.

The start of the revolution — We needed a changed attitude in teachers and pupils. The major change was the introduction of experimental work. Students were less conservative than teachers and we concentrated on providing materials for students to use wherever they could. We on providing materials for students to use wherever they could. We started in 1952 by making a chemistry kit, and students who purchased it received a journal with suggestions and directions for experiments. It receives a journal with suggestions and brought the kit to school to students began to ask questions and brought the kit to school to students began to ask questions and brought the kit to school to students began to ask questions and Brought the kit to school to students began to the form the first tution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them. The institution now known as the check what the teacher told them.

As we sold the idea of innovation to teachers so they began to request orientation programmes. Our teacher training project then started, with distribution of bulletins, pamphlets and journals, and summer institutes for work on laboratory experiments.

Innovation requires the involvment of leading scientists at the same time as high school teachers. It was a long hard fight to make science teaching in secondary schools respectable and important. High level manpower in chemistry is in extremely short supply, and our funds were limited. Selected professors visited the originators of the U.S. programmes and we decided that the CBAapproach would produce a larger initial impact. The text and laboratory guide were translated (and bound in one volume so that the practical work would not be skipped), and the foundation provided chemicals, glassware and other materials at reasonable prices. Teacher training in regular, high quality summer institutes then began and about 40 teachers each year became capable of using the CBA programme efficiently.

Science education centres Expansion of the teacher training programme for the new curricula led to the formation of Science Centres supported by the Ministry of Education. Six of these centres now provide teacher training through the summer institutes, in-service institutes and long term training programmes.

Publishing house A single curriculum is dangerous - it can become fossilised - so CBA was followed by CHEM Study which is now being introduced very rapidly. This added the new function of publishing to the other activities of our Institution. When we started, no commercial publisher was willing to gamble on the innovations. Initially, two of the larger university presses were organised to fulfill the programme. Today, the large publishing programme includes a new title each week, and over 500,000 copies a year. It has been transferred to commercial publishers but remains under the control of our Institution. This control includes the introduction of alternative texts, built - in laboratory guides, and stopping or changing old editions even when they are still being sold. Royalties return to finance other activities - e.g. teachers' guides, training and research into new ideas. The CBA preliminary edition is being replaced this year by the final edition and CHEM Study is also being published this year. The British Nuffield Project

Organic chemistry is a special problem as it traditionally forms part of the Senior High School programme and is all the organic chemistry that the biology students obtain. Some basic semi-micro experiments were introduced into our lab guide as alternative experiments.

Fieser's Chemistry in Three-Dimensions was translated and printed, and models were supplied. A larger programme in organic chemistry is now being planned under the direction of two full professors from the University of Sao Paulo.

General science education for children between the ages of 11 and 15 precedes the teaching of chemistry, and a new project is now widely used in the first two years of Junior High School. Topics discussed include air, water, fire, life, universe, chemical reactions, gravitation, heredity and animal diversity. Chemistry forms part of several chapters of the textbook which is written in such a way that students cannot proceed unless they do the experiments. Only simple materials are needed and kits are available.

A new project for general science that will include social science will be centred around conservation - conservation of matter, energy, species, human heredity and social structure.

Pocket book kits We are still trying to promote interest in chemistry as an experimental science. A new, successful idea is the kit which looks like a pocket book and contains a lively booklet and materials for the experiments suggested. It costs less than two dollars and is spreading rapidly. Some of the chemistry kits, with others in the spreading rapidly. Some of the chemistry kits, with others in the spreading rapidly and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics are new field - primary areas of physics are new field - primary areas of physics are new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics and biology have opened up a new field - primary areas of physics are new field - primary areas of physics areas of physics are n

Examinations The college entrance examination became an important innovation tool, and for about ten years I have been using the entrance examination for the Medical School of the University of Sao Paulo, examination for the Medical School of the University of Sao Paulo, which attracts large numbers of students, as a device for applying which attracts large numbers. Major changes in programmes pressure for curriculum changes. Major changes in programmes resulted from successive small changes. A practical examination resulted from successive small changes. A practical examination resulted from successive small changes. A practical examination Research in student selection by studying the tests (distribution, Research in student selection by studying the tests (distribution, reliability, correlation among the different subjects), and vocational reliability, correlation among the different subjects), and vocational reliability, correlation among the different subjects), and vocational reliability, correlation among the different subjects of the oldation at the second college teaching and innovation at this level is now demanded.

Other projects A project for biochemistry has been completed and published. We are concerned about instruments not made locally and we are designing low cost items for student use - pH meters, magnetic we are designing low cost items for student use - pH meters, magnetic stirrers, glassware etc. A photocolorimeter, a visible spectrophotometer stirrers, glassware etc. A photocolorimeter, a visible spectrophotometer and other electronic equipment are available. Our role is to create and other electronic equipment are available is too small to attract a market, and to manufacture when the market is too small to attract private enterprise.

Recent Developments in Chemical Education in Canada by $\operatorname{Brian} T_{\:\raisebox{1pt}{\text{\circle*{1.5}}}}$ Newbold

The responsibility for secondary education lies with the governments of each of the ten provinces and two territories. The departments of education in the provinces have curriculum sections which devise the programmes taught in high schools. Considerable changes in the chemistry curricula have been made in the last five years, greatly stimulated by the Chemical Institute of Canada. Dr. Newbold discussed the changes in each province in his paper and some of the highlights are summarised here.

British Columbia A student may now take two courses in chemistry (grades 11 and 12) instead of the one previously offered. Students in the academic technical programme are required to take one science course (biology, chemistry of physics) during their last two years. In addition, students taking a science or technical speciality are required to take a science course 12 along with mathematics 11 and 12. The CHEM Study text is prescribed for the new course. It has been divided into a 2-year study, each year being supplemented with additional information and experiments. The first part (chemistry 11) who have to meet the minimum science requirements in an academic specialising in science is more demanding.

New general science courses have also been introduced in the junior secondary grades of the high school - 8, 9, and 10. The chemistry content of these courses is Science 8: Chemistry of the Molecule; Science 9: Chemistry of the Atom and Science 10: Chemistry of the Ion. The study of chemical systems is developed in each of these courses with emphasis on (a) the descriptive aspect, (b) the quantitative aspect and (c) the particulate aspect - the use of the concepts atom, ion, molecule, electron in the description of matter

Alberta The CHEM Study programme has been authorised from Grades 10 to 12. After trials the order in which the material is presented has been changed from that in the textbook. In future Science 10 will contain Chapters 1 - 6; Science 20 (Grade 11) Chapters 13 - 17 and Science 30 (Grade 12) Chapters 7, 8, 9, 12, 18 and 19. In-service training of teachers presents a formidable task

and there still remains a sizeable number of teachers who are not familiar with the philosophy of the recently developed chemistry programmes.

Manitoba Chemistry is taught to Grade 11 and 12 students. In September 1968 a Physical Science Programme will become mandatory for Grade 10, and the CHEM Study programme mandatory for Grade 11.

Three major chemistry programmes are available in Ontario high schools. Industrial chemistry, a 2-year course, is offered as an optional subject to Grade 11 pupils enrolled in the 4- or 5-year programmes of the science, technology and trades branch. This course consists essentially of a study of fundamental chemical principles and their application to various aspects of the chemical industry. Strong emphasis is placed on student-performed laboratory experiments throughout the 2-year course. A course in general chemistry is available to students in Grades 11 and 12 of the 4- and 5-year programmes of any one of the three branches arts and science, business and commerce, science, technology and trades. A curriculum committee has been revising the industrial chemistry course and an experimental version of this revision should be ready for testing in September 1968. A study guide for teachers will be prepared as the testing proceeds. A new curriculum for Grade 13 is being introduced based on a modified CHEM Study programme (graduation from Grade 13 is a normal requirement for university entrance,). Examinations at Grade 13 level, formerly set and marked by the Department of Education are now to be controlled by the schools, and this should allow fora wide range of curriculum developments within the broad framework laid down by the Department.

Quebec This mainly french speaking province has a high school system more complicated than that of other provinces. A recent Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of education in the Royal Commission of Inquiry to examine the state of educat

The Chemical Institute of Canada The survey of Chemical Education Division of carried out by a committee of the Chemical Education Division of the Institute played an important role in stimulating change. The journal Canadian Chemical Education published by the Institute is distributed Canadian Chemical Education published by the Institute is distributed nationally and is proving to be highly popular with the teachers for whom it is intended.

Implementing the Nuffield Programme in England

by G. Van Praagh

Books Nearly 50 books were written by almost as many authors during the three years 1962 to 1965. Most of them were printed during the year 1965 - 1966 although some are still in production and are due for publication in 1968. Over 10,000 books for teachers have been sold and about 120,000 copies of the pupils' Laboratory Investigations.

Training of Teachers During the three years of the Project about 200 chemistry teachers were involved in compiling the course and and trying out sections in their schools. The communication of the results of the trials to the rest of the teaching profession was tackled in a number of ways:-

- 1. Residential courses lasting one week some 1500 teachers have now attended such a course.
- 2. A series of television programmes was put out in the Spring of 1968. A series of films is being made by the Esso Petroleum Company depicting teachers who were concerned with the Project explaining how certain topics are developed and how they may be taught.
- 3. Two films in particular 'Exploring Chemistry' and 'Chemistry by Investigation', sponsored by industrial organisations, convey perhaps more clearly than books or lectures the sort of activities by the Nuffield Chemistry Project.

Laboratories and Equipment The project implies that more practical work will be done than has been customary in most schools. The equipment of school chemistry laboratories is such that most teachers could adopt the Nuffield approach without much difficulty. The main Time can often be saved by the use of direct-reading balances, by filtering under reduced pressure, by the use of the centrifuge etc. Smaller quantities are advocated and the sizes of simple glassware are standardised. The introduction of gas syringes has greatly being designed, Nuffield Chemistry would have implications for the discussion and laboratory work can proceed in the same room.

The implementation of the Nuffield Chemistry Examinations proposals depends, probably above all else, on the existence of suitable examinations at the end. An examination which merely tests retention of knowledge is unsuitable for assessing understanding in the pupil. The University of London set up a research group to produce questions designed to test the qualities which the Nuffield Chemistry team hoped their approach would foster in the pupils. Alternative papers in the General Certificate of Education at Ordinary-level were devised and the examination has now been taken by a fair number of pupils from the trial schools. All Examining Boards have agreed to provide suitable examination papers in the future. They maintain that their function is to examine what the schools teach, so our teachers are introducing Nuffield Science into their schools with confidence, knowing that there will be a suitable examination for their pupils at the end of the course.

The Nuffield Project came after a long period during which science teaching did not change radically, and will result, in all probability, in a major change whose repercussions may be uncomfortably great. In the future we must hope that some sort of uncomfortably great. In the future we must hope that some sort of uncomfortably great. It is encouraging to find Science Teachers' than periodic upheavals. It is encouraging to find Science Teachers' than periodic upheavals. It is encouraging to find Science Teachers' Centres being formed in England and we hope that, by running Centres being formed in England and by maintaining the development in-service courses for teachers, and by maintaining the development of chemistry eaching initiated by the Nuffield Project, these centres will provide the link between research into science teaching and its implementation in the schools.

Reform of Chemical Education in Italy

by A. Liberti

In Italy, as in many European countries, all education is controlled by the Ministry of Public Instruction and all changes in curricula must be approved by the Technical Commission of Parliament. A curriculum is specified for each type of school and this must be followed strictly. Optional subjects and special courses are prohibited.

The average age at which students begin to study chemistry is 15 to 16 years. In the humanistic, classics and scientific high schools from which most university students are drawn, instruction is limited to three hours a week for one year. Even in technical schools, except for professional institutes for the training of chemistry technicians, the average teaching time is only four hours a week.

Legislators feel that high school education should not be very specialised andmost of the curriculum-should be devoted to the liberal arts. This attitude is based on the assumption that only the classics exert a determining influence in developing the minds of students.

Chemistry teaching in Italy has been strongly influenced by the international educational activities of the Organization for Economic Cooperation and Development (OECD). To initiate reform, OECD and the Ministry of Public Instruction jointly sponsored a piloy experiment in chemistry in 1963. A syllabus was first established by a committee of university professors, Ministry Inspectors and high school teachers, andbooks - 'Chemistry Lectures', 'Manual of Experiments' and 'Experimental Guide for Teahers' were compiled. Next, teachers were selected, training courses were organised and piloy classes established in schools. The experiment has been in progress for three years; some 100 teachers have been retrained and about 5000 students have attended the pilot classes. The results are quite satisfactory. Teachers have found their teaching duties lighter and have therfore had more time for experimental work and or anising laboratories. Most of the students were enthusiastic about the new system. They enjoyed learning chemistry and their examination grades were quite high, usually averaging 80%.

Details of the Experiment CHEM Study material has been taken as a pattern and the Italian books draw freely from this with several changes and rearrangements. Our 'Chemistry Lectures' differ mainly in the order in which the subjects are introduced. We discuss the structure of the atom and the formation of molecules at an earlier stage. We give a different emphasis to topics such as equilibrium, solubility, redox reactions and the presentation of organic chemistry. The only serious criticism we have of CHEM Study is that it complicates the study of physics. It is not clear how much physics a student needs fully to understand the CHEM Study course. There is some difficulty in integrating pilot schemes in physics with those in chemistry.

We have added some new experiments to those given in the CHEM Study manual e.g. ampholytes, solubility, equilibria, complex ions, the chemistry of some transition elements and we have introduced chromatography into the teaching of inorganic chemistry.

Visual Aids The advisory committee for chemistry has encouraged the use of good films. Some American films, translated by the Ministry of Public Instruction have been distributed to schools and some CHEM Study films in Italian, sponsored by the Esso Co., will soon be available. The Ministry of Public Instruction and the National Television Network have presented a number of 'integrating' National Television Network have presented a number of restaurable channel during regular school hours. At the end of each lecture channel during regular school hours. At the end of each lecture pupils and teachers were asked to criticise the programme and its pupils and teachers were sent questionnaires before the content. In addition teachers were sent questionnaires before the programmes with suggestions for class discussions.

Chemical Education in Japan by M_{\bullet} Oki

Japan is divided into 46 prefectures, each with its own board of education which generally sponsors and controls high schools. In addition, local governments such as towns and cities have their own boards of education, and these sponsor and control primary and junior high schools. Above this system the Ministry of Education exercises strict control by issuing syllabi to specify curricula and their content. Compulsory education lasts for nine years - through six years of primary school and three years of middle or junior high school. Pupils enter the primary school at the age of 6. About 74% of pupils now go on to high school (85% in urban areas). A survey of national examinations carried out by the Ministry of Education showed that about 20% of the examinees (primary and junior high school) could not answer any of the mathematics questions. This may mean that the lower half of all students admitted into high school have practically no mathematical ability. We are discussing the possibility of dividing the high school courses and I myself think this is essential.

Although there is some elementary science in the primary school, the child does not encounter scientific methods of thinking until he enters the junior high school at the age of 12. Here our natural science courses are divided into two branches, one dealing with physical sciences - physics and chemistry - and one with earth sciences and biology. The minimum requirement is 140 class hours per year for each field.

In principle, the fact that the topics are interwoven and treated as a unified theme should make chemists happy. However, the result is not satisfactory in practice, and we are hoping that the new syllabus and textbook now being prepared will improve the situation.

High school lasts for three years and the natural sciences are divided into four branches - physics (five units), chemistry (four units), biology (three units) and earth sciences (astronomy, geology, geophysics - two units). These four branches are obligatory. One unit means one class hour per week for a school year of 35 weeks. Some units can be allocated to any subject by the school and it is a common practice for chemistry to take five units in high schools. Chemistry is usually offered in the first or the first two years.

The high school chemistry course is offered at two levels - A and B. Course A, requiring three units, is supposedly designed for students of ordinary ability. But since university entrance examinations are based on the subject matter of course B, nearly all students select B. Also most Japanese want to excel and therefore attempt to push themselves beyond their abilities.

The Science Education Promotion Law By the provisions of this law the state encourages local bodies to promote science education by

- 1. Setting up a well-rounded programme for the promotion of science education,
- 2. Promoting the improvement of content and methods of science education,
 - 3. Improving facilities and equipment
- 14. Setting up and implementing a programme for the in-service training of teachers as well as for the training of prospective science teachers.

Article 9 of the same law states that where local authorities intend to up-grade equipment which is below standard the state shall make a grant in aid amounting to half the cost. The implementation of this important law has led to the setting up of science centres in various districts.

Because funds are limited it cannot be said that the Ministry of Education is doing enough to up-grade education. Progress is being made, albeit slowly. The syllabi are expected to change every ten years, and lively discussions are held among members of the ad hoc committee organised by the ministry. Advice is sought from specialists - e.g. from the Association of Schoolmasters. Unfortunately liaison with the Chemical Society of Japan has not been close in the past, but we hope our views will be reflected in the next revisions.

The Chemical Society of Japan The Society established a Committee of Education in 1952. The committee has concentrated on high school education because at this stage students are introduced to chemistry by that name for the first time. Also we believe that chemistry by that name for the first time. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The committee career interests begin to crystallise at this point. The

A programme has been initiated for developing a new curriculum for chemistry teaching. Although the American CBA and CHEM Study programmes are well organised and acceptable they are not necessarily suitable for Japanese schools because of differences in educational background. The syllabus we recommend is reproduced in Appendix 3 (incorporated at the end of this section).

Teacher Retraining The next problem is refresher courses for teachers. We have a rather unique system - the so-called 'Science Centres' affiliated with the local boards of education and not controlled by the Ministry. So far 33 centres have been established, and many more are expected in the near future. The Ministry pays about half the cost of the building and half the maintenance.

I believe that everywhere in the world the teachers who attend refresher courses are those who need them least, and those who need retraining do not attend unless forced to do so. We hope that local authorities who control high schools will be able to persuade more teachers to attend the science centres.

In general, the space in these centres ranges from 1000 to 4000 square metres - the average being about 1800. The building contains laboratories, a small library, workshops for making teaching materials and classrooms for pysics, chemistry, biology and earth sciences. An astronomical dome is usually included, and many centres have greenhouses. The centre is equipped with analytical instruments and equipment needed in high schools, but, in addition, some research instruments, costing on the average about 55,000 dollars per centre areavailable to arouse the interest of including administrative and clerical personnel.

Long term courses for teacher retraining last from three to twelve months and attendance is limited to a few participants. There are many courses of 40 - 50 hours (one week). Seminars on new teaching methods such as CBA are usually given on a weekly basis. There are other one day or half-day courses, usually on a selected topic.

Examinations Every university or college sets its own entrance examination and this presents difficulties for the high schools. The Institute of Development of Ability offers national examinations but in 1967 only about 20% of students entering higher education took the tests. Some universities now accept these examinations but the number doing so is small. National examinations for university entrance are in the distant future.

Recent Developments in Chemical Education in Scotland by A.J. Mee

Secondary Education Entry is at the age of 12, and after a period of orientation the pupil is classified as a certificate or non-certificate course student. The certificate course lasts for four years. All students take science, including chemistry, physics and biology for the first two years of the course. Thereafter they may choose to continue science to the certificate level or they may drop it for other subjects. About 55% of the pupils continue with science and they normally take two subjects - the majority choice being physics and chemistry, but the combination of chemistry and biology is becoming increasingly popular. At the end of the fourth year the pupil may either leave school or, if he is intending to enter a university, college of technology or college of education, he may stay on for one or (usually) two further years.

Scotland has its own educational administration which acts independently of but in liaison with the system in England.

Recent Developments in Chemistry Teaching Revision of the chemistry and physics syllabus was initiated by the science inspectorate in discussion with leading science teachers. We tried to compose a syllabus which would rationalise the subject so that it was not necessary for the student to learn numerous facts by heart. This involved shedding a good deal of material, which the older school of teachers regretted, and the substitution for it of material which, according to some, was quite unteachable at school level. However, we think we have overcome the difficulties and teachers are finding that what appeared to be an impossible task is, after all, proving quite amenable.

Guiding Principles The first two hears of the chemistry course must be rounded-off in itself, since 45% of the pupils will not study the subject further. This course should give students who are not specialising in science a proper background so that they can understand the scientific matters that crop up in everyday life and can take an intelligent interest in them.

In the third and fourth years we try to develop these topics a little further in such a way that they will form a foundation for the fifth year which is really the pre-university stage.

These conditions have imposed some compromises. Thus we felt that before students left the study of science after two years they should have some appreciation of atomic structure, and know what is meant by isotopes, radioactivity, radioactive fallout and so on. They might then understand the frequent references to these terms in their daily reading and viewing. This meant that some work on atomic structure would have to be done purely on the basis of telling rather than on discovery, since at this stage the pupils can have little appreciation of the experimental work that lay behind our modern ideas on atomic structure. However students have already picked up a good deal of atomic physics by their general reading, and they do not find this particular section of the work very difficult. The outline of the syllabus is set out at the end of this section in Appendix 2.

Response to the New Syllabus The syllabus was first offered to schools as an alternative course in October 1962 and by September 1966 all schools in Scotland had decided to adopt it. In May 1967 two-thirds of the schoolshad reached the fourth year of the scheme and were presenting canditates for the Ordinary Grade Certificate. The eachers knew that examinations appropriate for the new syllabus would be set. We intend never to let chemistry teaching again get into the rut into which it had fallen. We hope that from now on there will be continuous revision of the syllabus every few years.

Assessment The teachers themselves favour the new courses. They find them more interesting to teach, although they are more time demanding in the preparation of assignment sheets and in the setting up of experiments and materials. The scheme really requires at least a laboratory assistant if not a technician in each school. Some authorities have now appointed laboratory assistants to their schools but they are not always easy to recruit. The pupils tend to be more interested and enthusiastic, but very much depends on the school and the efficiency of the teaching. Some teachers have said, however, the material presented to them, when they will learn it and reproduce it in examinations. This, they say, is particularly true of girls. Some teachers have said that the scheme is excellent for the better pupils but not as good for those less well endowed.

Recent Developments in Chemical Education in Scandinavia by G. Ahman

In recent years both Norway and Sweden have replaced their primary and lower secondary schools by a new, compulsory nine-year school course. In the lower and middle departments of the nine-year school simple chemical and physical processes are explained which relate to processes observed in everyday life. Pupils move to the upper department of the school in the seventh grade at the age of 13, and they begin to study chemistry as such at age 14 in grade 8. In a comprehensive school it is unrealistic to demand uniformity of performance. Education must allow for individual differences. Instruction should not be in terms of predetermined opinion, cause and effect; rather the pupils should acquire knowledge for themselves through their own work and experiences. Where this obtains, the teacher is a guide and adviser, a director of work rather than an instructor in the conventional sense.

The syllabus for chemistry in the nine-year school is rather traditional, and experience showed that the response of students to it left something to be desired.

The Project In the autumn of 1964 a joint Norwegian-Swedish project was set up with economic assistance from OECD. The aim was to test new currcula and textbooks by means of experimental teaching programmes. New textbooks for pupils and new guides for teachers in the comprehensive schools were developed. Self-instruction materials were provided including provision for laboratory work, home work amd supplementary work for gifted pupils. Two summer schools for chemistry teachers were organised and pilot courses for pupils were planned at selected schools.

The committee's aim was primarily to compile a modern syllabus for teaching chemistry in a mannerthat would capture the students' interest and stimulate their desire for further study.

Students work in small groups under supervision by the teacher. They work at a joint task or solve problems that are part of a joint project. The aim is to give an opportunity to work both individually and in cooperation with others.

Learning Studios Language laboratories adapted for instruction in other subjects are now called learning studios, and experiments have

been carried out to see if they can be used for physics and chemistry teaching. To be effective, the learning studio must be equipped with carefully designed teaching materials, and subject areas must be carefully selected. They will probably be of greatest value only for portions of a subject which are of fundamental importance but which are somewhat advanced and difficult for a student to understand. The material should be self-instructive, and usable for both remedial and advanced courses. Experiments have been under way since 1966 and the results are now being studied underthe supervision of experts in psychology and education.

Television The Swedish Broadcasting Corporation in cooperation with the National Board of Education started a television programme for pupils i their eighth year at the comprehensive school in 1966. The course consisted of 14 programmes, a textbook in two parts, guidance material for teachers and specifications for equipment and materials specially arranged for 30 laboratory experiments and 30 lessons. Although they are designed for teachers who lack special training in chemistry, the programme can also be used by trained teachers to save time, effort and to vary the type of instruction they give. The experiments shown in the TV programmes are selected because they are too costly for school laboratories, need special equipment or are difficult or dangerous for teachers to perform themselves. Animated cartoons are used as an aid in explaining complicated processes.

Industrial processes have been introduced by visits to plants, experiments and theoretical explanations. The results have been good and instruction, regardless of the teachers qualifications, has become increasingly effective. The programme is to be extended to the ninth year of the comprehensive schools. Requests have been received for evaluation of the material, for access to diagnostic tests and also for descriptions of individual tasks that can be assigned to pupils for performance between programmes. A general opinion prevails that a supply of of the programmes.

UNESCO Programs in Chemical Education

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UNESCO programs in chemical education aim to improve both the quality and the quantity of chemical education in UNESCO's member states. One major aspect of these programs relates to the needs of the rapidly changing countries in Africa, Asia, and Latin America. A series of UNESCO sponsored conferences of Ministers of Education held in these regions during the last decade, and the specialized meetings of experts which followed them, have indicated the need for an increased emphasis in the school curriculum on science education. One such conference, that of African Ministers of Education which was held in Addis Ababa in 1961 with a view to establishing an inventory of educational needs and a program to meet those needs, made the following analysis of the relationship between educational content and economic development:-

"One of the principal deficiencies of most edu-Cation systems (in Africa) is their tendency to give too little weight to studies based on the natural sciences. At the university, there are usually proportionately too many students of arts, law, and social science, and too few students of science, engineering, agriculture or medicine. At the secondary level there is a deficiency of technical institutes and farm schools, and the great majority of general secondary schools fails to make adequate provision for teaching the natural sciences. In the same way, the primary schools tend to neglect mechanical and biological studies. The chief reason for this is that the institutional patterns of education were formed many centuries before the modern technological revolution occurred, with its dependence on science. Education has therefore inherited its traditions and prejudices from a pre-scientific age. If education is to be integrated with economic development and is to pay its way in purely economic terms, one of the principal changes must be a shift in curricula away from philosophic and literary studies towards natural science and its various applications. Entire substitution of one for the other is not in question; but a shift in relative proportions is of great importance". (Addis Ababa Final Report, page 10.)

Science teaching is seen as important not only in relation to economic development but also as an essential part of contemporary culture. Many so-called developing countries realize the need for all their citizens to become scientifically literate if they are to become attuned to modern society.

UNESCO programs place particular emphasis on the development of modern approaches, techniques and materials for science teaching. With regard to such activities, UNESCO is in a unique position to act both as a catalyst and as an "internationalizer." Three areas of particular importance for any expanded and improved program of chemistry teaching are: the provision of chemistry teaching facilities and materials including opportunities for teachers to try out new materials, the training of chemistry teachers, and chemistry curriculum reform. Closely linked with these is the in-service training of teachers and the dissemination of information on modern trends to leaders of chemical education and, in particular, to "teachers of teachers". UNESCO has major programs in all these areas.

1. FACILITIES FOR CHEMISTRY TEACHING

With financial assistance from UNICEF, many programs are being developed in Africa and Asia for improving science teaching facilities. One notable example is a project, planned in Ceylon, not only for supplying equipment, but also for establishing a factory where scientific apparatus can be manufactured and repaired locally. UNICEF is providing aid in the form of equipping laboratories and with supplying materials for chemistry teaching in Korea, Pakistan, the Philippines, India and Taiwan in Asia; in Congo-Brazzaville, Ghana, Nigeria and Sierra Leone in Africa, in Brazil and Honduras in Latin America, and in Iraq and the Yemen in the Arab States, to name a few countries. One of the major emphases in the new chemistry program is on pupil experimentation. Requests have been received by UNICEF from several countries who wish to try out modified versions of programs such as CHEM Study and Nuffield Chemistry, for the equipment of pilot classes to carry out the chemistry work demanded by these programs.

2. THE TRAINING OF SCIENCE TEACHERS

One of the most urgent needs for an expanded science teaching program is a supply of well trained teachers. Financed by the United Nations Development Program, a large program of training colleges for secondary school teachers has been embarked upon recently in Africa and is being extended to Asia. Twenty such colleges have been established in Africa. In each of these, science teaching plays a prominent part. Many of these colleges are attached to a university. Experts who are college professors are recruited to work in the university science faculty and to provide the course content needed to train teachers to first degree standards in science. At the same

time, education experts provide pedagogical training, and a program of teaching practice is carried out in local schools. Every effort is made to recruit staff for such colleges, acquainted with newer approaches to science teaching, so that they, in turn, can train their students in modern methods.

Another UNESCO program aims to provide further scientific training for staff members of the universities and scientific institutions in developing countries. Several countries with long established scientific traditions are collaborating with UNESCO in organizing a network of UNESCO sponsored international postgraduate courses in science subjects which provide both theoretical and practical teaching as well as initiation to individual research in selected areas of pure or applied science. The post-graduate training programs involve, in particular, methods and techniques in scientific investigation. A course on the subject of advanced techniques in analytical chemistry is being held at Charles University, in Prague; courses concerned with chemistry and chemical engineering are being held in the Federal Republic of Germany and in Japan. Fellowships and training grants provided by UNESCO enable selected chemists from many countries to attend these courses.

3. CURRICULUM REFORM

The need to modernize the chemistry curriculum and to adapt it to local needs is a matter of pressing concern all over the world. The establishment of curriculum reform projects such as CBA, CHEM Study, and Nuffield Chemistry Projects has stimulated many countries to reappraise their chemistry teaching. Developing countries who wish to initiate their own programs of curriculum reform in the sciences do not have sufficient funds at their disposal, and are turning to UNESCO for assistance.

3.1 Exchange of Information

One form of assistance is through publications. A serious problem facing chemistry teachers in universities, training colleges and high schools is that of keeping abreast both with modern developments in chemistry and with its teaching. A volume of articles from a wide variety of sources on fundamental chemistry theory and chemistry teaching entitled "New Trends in Chemistry Teaching" is being published biennially (see p. 29). This publication and "A Source Book for Chemistry Teaching" which is in the process of being compiled, have received support from the International Union of Pure and Applied Chemistry (IUPAC) Teaching Commission which acts as a principal adviser to the whole of UNESCO's chemistry teaching program. A comparative survey of chemistry teaching in six European countries has been drawn up in mimeographed form and will be revised shortly for publication. In addition, studies on science teaching in selected countries in Africa and Asia have been carried out under the auspices of regional programs. The Bulletins of the UNESCO Regional Offices for Science and for Education also supply information about new developments in science teaching in their respective regions. In addition, chemistry journals from the USA and Great Britain have been made available in several developing countries either free or at reduced rates for the benefit of schools and universities.

3.2 Pilot Projects

To help relieve the problems of scarcity of science teaching materials and inadequate preparation of science teachers in developing countries, UNESCO has supported experimental pilot projects in the basic sciences. These projects aim to provide scientists and science educators in a particular region of the world with an opportunity to

think through their problems in the teaching of a particular science, and also to draw on the expertise of world leaders in the reform of the teaching of this science. Two such projects have already been held, for Physics in Latin America, and for Chemistry in Asia. A third, for Biology in Africa, is just starting. In such projects, about twenty teachers from universities and teacher-training colleges gather to work for a year under specialists to study and develop resource materials in the particular science.

From September 1965 through July 1966 the UNESCO Pilot Project for Chemistry Teaching in Asia, composed of twenty chemistry teachers from universities and teacher-training institutions of fifteen Asian countries, convened at Chulalongkorn University in Bangkok. During this first year of the Pilot Project, the group made a critical study, referred to as content analysis, of two broad topics in chemistry: chemical stoichiometry (see p. 35), and energy and chemical reactions. Laboratory research has been carried out with many chemical systems in order to devise laboratory experiments for students. Teaching materials including programmed teaching sequences and 8mm film loops prepared by the group, have been distributed to study groups in each participating country in Asia. These study groups, composed of chemistry teachers from schools and universities, are utilizing the teaching materials as resources for further local development of textbooks, teachers' guides, and for conducting in-service courses for chemistry teachers.

In the second phase of the project which started in November 1966 and is still continuing (see p. 32), further resource materials have been developed. A month's summer institute for Thai teachers was held, centered particularly round the subject "compound formation". Various aspects of

the subject were taken up by the lecturers, who were drawn from several Asian countries including Japan, Ceylon and Thailand, and also from Australia, Czechoslovakia, U.S.A. and Great Britain.

3.3 Assistance to Governments

In conclusion, it should be mentioned that many university scientists and science educators are working as UNESCO advisers on science teaching to Ministries of Education in developing countries. These specialists are financed chiefly by funds from the United Nations Programme of Technical Assistance. They spend one or more years assisting governments with devising new curricula and examinations, re-training teachers, and establishing curriculum reform groups. In Asia, several such experts have assisted with developing Pilot Project Study Groups and are working with chemists who have participated in the Chemistry Pilot Project. A special briefing room has been organized in the UNESCO building in Paris where these specialists can find a choice of the most up-to-date science teaching resource materials available, such as reference books, manuals, teachers' guides, laboratory kits, and audio-visual equipment.

Organization of Secondary Education in England and Scotland

ENGLAND		SCOTLAND				
Year of secondary course	Age	Exam.	Year of secondary course	Age	Exam.	Comments
1	11+		: 			
2	12+		1	12+		All pupils take science for
3	13+		2	13+		years 1 and 2
4	14+		3	14+		About 55% continue with
5	15+	O level	4	15+	O grade	science to O grade
			1-0			
6	16+		5	16+	H grade	About 70% of those tak-
7	17+	A level	6	17+	(Post-Higher	ing science at O grade continue to take science
8	18+	University Scholarships etc.			Certificate) University Bursary Completition, or English A levels	at H grade

Entry to University at end of year 7 or year 8. University course 3 years.

Entry to University possible at end of year 5, but normally at end of year 6 University course 4 years.

Scottish Education Department Outline of Alternative Chemistry Syllabus

One general aim of the syllabus is to give pupils an understanding of how and why chemical reactions take place and how fast and how far they go. This involves some study of atomic and molecular structure and energetics. The other aim is to give some idea of the vast social importance of chemistry.

Teachers are, of course, at liberty to change the order of the scheme in any way they like, but the order has been carefully worked out as a possible logical teaching order.

The following is intended to give merely an outline of the syllabus and does not mention every topic included.

First Year. Age 12-13.

Section 1. An opening "romp" in which the pupils are introduced to chemical reactions and some of the "tools" by which they are brought about. The use of heat, of light, and of electrolysis for bringing about chemical changes are illustrated. We have all come across the fact that, when boys and girls first enter the chemistry laboratory, they do so thinking that it is a marvellous place where they will be carrying out wonderful experiments, and they very quickly become disillusioned. If we could only maintain the interest which is obvious when they first attend a chemistry class we should be well on the way to obtaining more science students at the later stages of the course. We give the pupils the opportunity of carrying out a number of chemical reactions, usually very spectacular ones, in which they get a general idea of the way in which reactions are brought about.

The pupils are *not* expected to learn very much factual material from this section. They will, however, discover for themselves that in many chemical changes heat is evolved, and that in order to initiate chemical change it is often, but not always, necessary to supply energy. This is the beginning of the appreciation of energetics.

Section 2. The Particulate Nature of Matter. The pupils carry out experiments which lead them to believe that the only reasonable way to explain the behavior of matter is to assume that matter is particulate. It is important that they should see that the atomic theory is a

guess, but it is a very good guess. This section continues with work on solutions, crystals, distillation, chromatography and colloids.

We find that the large majority of our pupils already know that matter is atomic, and they think that it is unnecessary for us to attempt to show that this is the case. However, we feel that it is desirable that this work should be put on a true scientific basis, particularly because we want them to realize that the atomic theory is a guess, that no one has ever seen atoms, and that no one ever will. Thus the atomic theory is purely an idea in the mind of man to explain the behavior of matter. And so we introduce them to a number of experiments which cannot be explained reasonably except by supposing that matter is atomic.

Section 3. The Atmosphere. This is dealt with through a consideration of combustion.

In order to drive home ideas of energetics at an early stage, we no longer put any emphasis on a chemical method of making oxygen in the laboratory. We normally obtain the gas from a cylinder in just the same way as we would take another chemical from a bottle. There seems to be little need for spending time on the preparation of common gases unless the reactions involved in their preparation are of some importance. It may be argued that the preparation of oxygen by heating potassium chlorate and manganese dioxide is of value in that it introduces catalysis. The better reaction for this purpose is probably the catalytic decomposition of hydrogen peroxide. The properties of oxygen and nitrogen are studied particularly from the point of view of the reactivity of oxygen and the inactivity of nitrogen. Although at this stage we do not pretend to explain why there is this difference in reactivity, this does start the pupils thinking about the reactivity of substances in general and leads them on to the reactivity series. We burn a number of substances in oxygen and observe the vigor of the reaction, and in this way we try to put the various elements in some sort of order of reactivity in terms of their combination with oxygen. It is obvious, of course, that this is a very crude way of listing reactivities. Nevertheless, it is the beginning of the idea, and this is going to be refined throughout the course until eventually we arrive at the electrochemical series.

Second Year. Age 13-14.

Section 4. Water. We show that water contains hydrogen by the reaction of certain metals with water and also by electrolysis. We show that hydrogen will combine readily with oxygen and possibly it will be able to remove oxygen from certain or perhaps all metallic oxides. The pupils try a number of metallic oxides and find that hydrogen will only reduce some of them. Here again we can get the idea of reactivity series which can link up quite easily with the readiness with which metals and nonmetals combine with oxygen.

Section 5. The Earth. We study the earth and the minerals obtained from it. We use the ideas of reactivity that we have deduced earlier on in connection with oxygen and nitrogen. We wonder why it is that only certain metals occur native and we can see that this is linked with the readiness with which they combine with oxygen. We observe too that certain metals occur as oxides, others as sulfides, and comparatively few, as carbonates. We wonder why this is, and we then go on to show that carbonates can be thermally decomposed. We show that some carbonates are very readily decomposed, others are not. Why is this? The answer is connected again with the reactivity series. To conclude this section on the earth we deal to a slight extent with the formation and nature of coal and oil, although these topics may come up again when we consider fuels.

Section 6. The Sea. The salts dissolved in sea water are identified, and the properties of chlorides, bromides and iodides are studied. The idea of a family of elements is introduced.

All this time there will have been a chart of the periodic table in the laboratory which will have been referred to from time to time and pupils will now see that the families of elements occur in the vertical series. Section 7. Atoms and Molecules. To finish off this section of the work, we now have to introduce the idea of atomic structure, and, as stated earlier, this is perhaps the least satisfactory part of the first two years of the course. Much of this part of the work cannot be backed up by experimental observations and it has to be dealt with more or less as lecture work

The constituents of atoms—electrons, protons and neutrons are introduced. Pupils know from physics that electrons are constituents of all matter. The idea of isotopes; the discovery of radioactivity and the nature of radiations from radioactive materials are dealt with.

This work is included because a considerable num-

ber of pupils will be dropping science at this point of their school career, and it is considered advisable that all should know the meanings of terms such as "isotopes," and "radioactive fall-out."

Third Year. Age 14-15.

Pupils continuing the study of chemistry in the third and fourth years will be those who have decided that they will be taking the subject either at Ordinary or Higher Grade in the SCE examination.

Section 8. Chemical Combination. Experiments on electrolysis lead to deductions about the existence of ions in certain types of compounds, but not in others. Experiments on the migration of ions. Electrovalent (or ionic) bonding is contrasted with covalent bonding. At this stage we do not complicate matters by indicating that these are only the ends of a gradation. Chemical formulae and equations are introduced, and calculations involving them are dealt with. The mole concept is introduced for the first time.

Section 9. The Electrochemical Series. Displacement of one metal by another is dealt with in ionic terms. Corrosion and protection of metals. The idea of electrode potential is introduced as a measure of readiness of a metal to form ions in an aqueous medium. A distinction is drawn between electrode potential and ionization potential. The electrochemical series is compared with the reactivity series. Oxidation and reduction are introduced as transfer of electrons.

Section 10. Acids, Bases and Salts. Characteristics of acids are investigated and pH is introduced merely as a scale of acidity. The process of neutralization is followed by conductivity apparatus as well as by the use of indicators. Heat of neutralization is determined and shown to be the same for all neutralizations involving strong acids and bases. This leads to the realization that their neutralization is merely $H_3O^+ + OH^- = 2H_2O$. Ionic interchange and precipitation is followed by conductivity experiments. General methods of preparing salts are considered.

The following sections (11-16) deal with chemicals in common use. Their study is based very much on ideas which have already been developed on bonding and on energetics. Thus, by the end of the fourth year pupils should have some appreciation of the part that chemistry has to play in everyday life including its world-wide significance in economics, such as in matters of the relief of famine, in petrochemistry, in the building industry, and in the manufacture of construction materials. We consider this to be an important part of any chemistry course. It should not be so academic

that it neglects the part that the subject has to play in the everyday life of the individual.

Section 11. Sulfuric Acid. The manufacture of sulfuric acid from sulfur dioxide and the main properties and uses of the acid.

Section 12. Nitric Acid. The preparation of ammonia from atmospheric nitrogen and its conversion into nitric acid. The reactions of nitric acid. The importance of sulfuric and nitric acids in the fertilizer industry and a study of the nitrogen cycle complete this section.

Fourth Year. Age 15-16.

Section 13. Fuels. Gaseous and liquid fuels are studied (coal will probably have been dealt with in section 5). This section gives an opportunity to introduce organic chemistry. The homologous series of hydrocarbons, catalytic cracking of oil, and the synthesis of hydrocarbons are considered.

Section 14. Foods and Related Compounds. The nature of carbohydrates, proteins and fats. Also included are the hydrolysis of starch, the fermentation of glucose, the use of fats in the manufacture of soap, and the preparation of detergents.

Section 15. Macromolecules. The process of polymerization, natural and synthetic polymers, the recognition of various types of plastics, and the nature of silicones. Section 16. The Halogens. This is an extension of work done earlier on this family of elements and includes explanations of reactions in terms of the theory developed in sections 8, 9 and 10.

This concludes the work up to Ordinary Grade. Those pupils proceeding to universities and other centers of higher education will continue to study the subject for a further year and will take the Higher Grade examination, particularly if they intend to study science at these institutions. The syllabus for this additional year is as follows:

Section 17. Chemical Theory. The approach here is based on the use of the mass spectrometer for the determination of atomic and molecular masses, and leads to the deduction of Avogadro's Law by a combination of these results with the laws of electrolysis and the densities of gases. Thus Avogadro's assumption is no longer a hypothesis but has the standing of a law (this was usually assumed in the traditional approach). The circular arguments which were of frequent occurrence in the traditional treatment are avoided.

Section 18. Further Development of Valency Theory. Periodic Table. It is now pointed out that purely ionic and purely covalent bonding form the extremes of a

continuous scale. The nature of interatomic and intermolecular forces are more fully considered. The elements 1-20 of the periodic table are considered to bring out the importance of electronegativity, atomic and ionic radii, etc., with particular reference to hydrides, oxides and chlorides. Oxidation and reduction are dealt with more fully than before.

Section 19. Chemical Reaction. This is the culmination of this part of the course in that we are now able to obtain some answers to the questions we set ourselves at the beginning: what makes a reaction go, how fast does it go, and how far does it go? Reactions are considered as collision processes. The effectiveness of collision is considered from the points of view of orientation and activation energy. The reason why endothermic reactions are possible is based on simple considerations of enthalpy and entropy, the latter being dealt with entirely on the basis of randomness or organization. The speeds of reactions and the factors influencing them are dealt with from the experimental angle entirely and this leads to the consideration of catalysis and equilibrium.

Section 20. Carbon Compounds. To round off the course some reactions of functional groups in carbon compounds are dealt with. After the hydrocarbons themselves have been considered we pass on to the reactions of the -OH,>C=O, -CO₂H, and -NH₂ groups. Some practical knowledge of the behavior of organic chemicals is held to be necessary before much is attempted in the way of mechanisms, and the aim of this section is to give students this practical acquaintance with the subject.

The Proposed New Japanese Chemistry Curriculum

Chapter 1. Heat and Substances. Discusses various changes resulting from applying heat to materials, but a thorough treatment is not intended here. At first, phase changes are demonstrated by heating or cooling several materials—for example, benzene, naphthalene, and water. Thus students are introduced to the scientific method and led to consider the degree of purity which in turn depends on accuracy of technique. Next, students observe changes caused by strong heating and burning, and study the products of combustion. Laws of definite proportions and conservation of mass are treated briefly.

Somewhere in a chemistry course, students must of course, think by themselves about what chemistry is. Ideally, this should be left to the last, but on the other hand, it might not be wise to teach students without letting them know the purpose of the course. As a compromise we decided to put a section on this subject at the end of the first chapter.

Chapter 2. Properties of Gases. Various gases are introduced. Weighing a constant volume of several gases as in the CHEM Study course is a good introduction to the fact that varieties of gases exist. Pressure-volume-temperature relationships are treated and absolute temperature is introduced, but the ideal gas is not touched upon.

Chapter 3. Molecules and Atoms. Explains properties of the gases discussed in chapter 2. That molecules are responsible for these properties is stressed and Avogadro's number is introduced. Then the concept of molecular weight is discussed, followed by atoms as components of molecules. Chemical elements as the components of matter are introduced.

Chapter 4. Periodicity of Elements. History of the periodic table is discussed, using the long form as the standard. Then a method suggested for stimulating independent thought is to question the reason for leaving the upper middle part of the table blank. This of course is related to atomic structure and, when this subject is reached in the last part of the chapter, it should be interesting for students to recall the blank places. In this chapter, the periodic table is viewed from top to bottom; view from left to right is presented later.

Chapter 5. Periodic Table and Properties of Substances. At this point, general properties of compounds are taught because the students will have developed sufficient understanding of classification of materials. These are presented as metallic, ionic, and molecular. Thinking that a chapter on transition metals would not be necessary, these metals are introduced here from the standpoint of properties. Intermolecular forces are presented also.

Chapter 6. Acids and Bases. These are introduced in relation to the periodic table, but treatment is rather qualitative because the students have not been introduced to dissociation equilibria. They merely observe ionization of acids and bases. Neutralization is defined with respect to quantitative analysis of acids and bases but the classical definition of a salt is omitted. Lewis theory of acids and bases might be treated, but we consider this optional.

Chapter 7. Oxidation and Reduction. Oxidation is defined as loss of electrons, and reduction as the gain of electrons, but the classical definition—reduction as gain of hydrogen or loss of oxygen—will be presented also because some examples are difficult to understand in terms of electronic shifts. Next the electric cell is explained in terms of loss and gain of electrons and oxidation potentials are presented. Hopefully, students will understand why the so-called oxidant is oxidized sometimes when mixed with other materials. Use of oxidation numbers is limited to instances where they can greatly facilitate understanding.

Chapter 8. Phase Equilibria. Chapter 1 is reviewed here because important functions of materials have been dealt with in the two preceding chapters. Now the students seem ready to understand the concept of energy, and it is stressed that at the same pressure, heating is necessary to vaporize liquids and liquefy solids. Relationship between thermal energy and temperature is discussed and the definition of boiling point is taught from the standpoint of kinetic energy. As a natural consequence of these concepts, vapor pressure and latent heat are presented.

Chapter 9. Solutions. The role of solvents is discussed. Because the students do not know polarity at this stage,

expressions such as "a substance is soluble in a like substance" is used and to understand the problem they wait until chapters 13 and 14. Solvation is also discussed to help in understanding dissolution equilibria, and the concept of entropy is introduced but not by that name. Much discussion was centered on whether or not colloids should be included. Because these are encountered in everyday life, they were included but on an optional basis.

Chapter 10. Chemical Equilibria. Now the students must be ready to understand equilibration. Free energy is introduced, but not by that name, because we prefer to explain equilibria using concepts of entropy and enthalpy. Conservation of energy must be treated, and this necessitates introduction of potential energy. We now can discuss dissociation equilibria quantitatively and the equilibrium constant is introduced.

Chapter 11. Reaction Rates. That reaction rate is different from velocity of movement must be emphasized because in Japanese the same word is used for both. It is pointed out that a chemical equation is a balance sheet of total reaction, and thus reaction mechanisms are introduced. The effects of concentration and temperature on reaction rates are discussed and also first and second order reactions, but analysis is limited to first order systems.

Chapter 12. Structure of Atoms. This chapter plus 13 and 14 discuss some finer details of chemistry. First, electrons and atomic nuclei are introduced and also the hydrogen atom from the standpoint of quantum mechanics. Principal quantum numbers are given and the periodic table is examined again, this time in terms of atomic structure.

Chapter 13. Covalent Bond and Electronegativity. Here, the hydrogen molecule is discussed briefly and some molecular materials are presented and linked to chapter 5. Covalent bonds involving fluorine are discussed with respect to the atoms from right to left in the second row of the periodic table. This series of compounds is an excellent example for introducing electronegativity and then polarity and boiling point of some compounds. Stereochemistry of some compounds and double and triple bonds using ethylene and acetylene as examples are introduced. In this connection benzene can be presented as a molecule having wholly overlapping orbitals. Coordinate covalent bonds and the hydrogen bond are discussed briefly.

Chapter 14. Ionic and Metallic Bonds. Begins with discussion of crystals of sodium chloride followed by other ionic crystals. Thus salts are defined as materials constructed by ionic bonds which means that in terms of

some materials our definition is rather ambiguous. Polyatomic ions are presented and, after discussing some reactions involving ions, metallic bonds are treated briefly. Chapter 15. Chemistry of Third Row Elements. Elements in the third row of the periodic table are discussed. The d orbitals are introduced by saying they are involved in chemical bonding, but the geometry is omitted. The periodic table is examined reading from left to right in order to point out the tendency of change in properties of compounds. Thus, halides, hydrides, oxides, hydroxides and oxy-acids are presented.

Chapter 16. Structure of Organic Compounds. This and the next chapter are devoted to organic chemistry. This chapter treats the basic structure or skeleton of organic molecules including stereochemistry and isomerism. Why there are so many organic compounds although their skeleton contains only carbon and hydrogen is explained.

Chapter 17. Properties of Organic Compounds. Rather than classify organic compounds as aliphatic, aromatic, and heterocyclic, we prefer to classify in terms of functional groups because these are central to organic chemistry. Thus alcohols and phenols are treated in the same section. Differences in properties such as solubility in aqueous alkali is not important because alcohols also dissociate to some extent.

The following chapters are optional and can be presented if time permits.

18 Polymers (natural and synthetic)

19 Substances of Biological Origin

20 Isotopes and Radioactive Elements

21 Water

22 Procedure of Chemical Research

23 Chemical Calculations

EXAMINATIONS/EXAMENS

Examinations

J. Arthur Campbell Harvey Mudd College, Claremont, California

If this were the first session of the conference instead of the last, each of you would now be taking an examination. The most effective way to discuss examinations is to try a little role reversal and have each of the teachers who is normally engaged in designing examinations sit down and take one. This is the way we normally begin the summer institute programs with which I am associated. If I had to defend our summer programs I would put very high on the list of defenses that teachers occasionally have to sit where students normally sit, so that teachers may learn what their students have to put up with all the time. Someone here suggested that it would be very unfortunate this morning if I gave an examination. Now your students feel that way every day. The question is, of course, would they study if they didn't feel this way? It is just possible that they might feel a lot better about studying if they were not being threatened with examinations.

Personally I don't think examinations are important in a general way but I find I am in the minority here. I have come to realize that for most people; students, teachers, administrators connected with the teaching process, the examination is by far the most important thing. A very large part of the educational system in this country, and everywhere else I have visited, is examination oriented. The student exists to take the examination, the teacher exists to teach the student to take the examination, and, through the student doing well, to satisfy the teacher's ego and perhaps even get a pay-raise. The administration exists to give exams to prove the student learns something to justify

the system so that next year they can give more examinations to prove the system has done something to justify the system. I'm not trying to be cynical, I'm trying to be truthful. I am sad that it is true and everyone else I have talked to is sad that it is true also, including people who are the most ardent supporters of the examinations system.

I have an increasingly firm conviction that the way to change is not to change the syllabus or write a new text unless at the same time we change the examinations. If I were given only one thing I could do to change an educational system I would apply a little physical chemistry and would decide that the rate determining step is the examination and, therefore, I would attack the examination system. It is possible to attack the exams in such a way over a course of three or four years that you can almost completely reorient a system without changing much of anything else.

Writing a syllabus is almost a complete waste of time. I base this claim on the experimental observation that when I look at syllabi or when other people look at syllabi they have absolutely no idea as to what is to go on in the course. In fact, two different people looking at the same syllabus arrive at two contrary conclusions as to what should go on in the course. I believe that syllabi are operationally defined by the examinations that are given at the end of the course.

On being asked several times recently to participate in making out a syllabus for a course, I have responded each time that I would participate if the syllabus would be amplified at least

to the extent of 500 to 1,000 typical questions, and, even more important, typical answers.

A syllabus alone is useless. A set of questions alone is useless. A syllabus plus a set of questions plus a set of suggested answers can be very useful. If you don't say what kind of response you expect how can you possibly hope really to communicate with the teacher? The examination fleshes out and makes a syllabus work.

I am very intrigued at how many people now are using so-called objective tests. For many years I was ardently opposed to them. In the 1930's when I was still teaching at the University of California at Berkeley I obtained one of the widely used objective tests. There were roughly 120 items on it. I thought 30 of them were terrible and wrote and said so. I was irritated when the test came out with my name on the cover as a person who had commented on it, because I thought the test was so bad it should never have been given and some of these 30 items were still on the test. It took me a long, long time to realize that objective tests were good for anything. In many ways objective tests have a great deal to offer, but it is folly to rely on any one kind of examination. Each different kind of examination has some merit and we ought to give the students a balanced diet.

Open-book Exams

I would strongly suggest that you experiment a little with what amounts to open-book examinations. It has been suggested that an open-book examination is too confusing because too much information is available to the student, and it might be almost as effective to give the student data tables. I don't agree. The student ought to have his book because the purpose is not merely to look up numbers. If a student needs a particular bit of information he can find it, but nobody has ever designed an open-book examination where the student can sit down and in the 50 minutes available to him look up all the answers. My own definition of such an examination is that the answers are not in the book, only ideas.

The Point System

A teacher at Purdue University had a very clever way of giving examinations to a relatively small class. Purdue trains many engineers and some of them become consulting engineers. This professor, therefore, during every examination set up a consulting system. He was the consultant. If a student was stuck on an examination question he could come and ask the professor anything he wished. The professor would then say, if I tell you the answer it will cost you ten points, or five points or three points. The student would then say yes or no. If the student thought it was worth the points, the professor would give him the full information. It was then up to the student to go back and finish the question. If the professor gave him the full answer to an examination question, he would say "that is going to cost you all but two of the points" realizing that most students would not be able to go back and write it down correctly even if he told them the answer.

I used to give examinations in which I would do an experiment before the students. I would give them half credit merely for writing down what I had done, just for correct observations. The other half would be for interpreting what I had done. It is remarkable how often students can't even report correctly the simplest observations. You should try it sometimes. Students are in a very strange state when they are taking examinations, and the more insight we can obtain about these states the better. You might also learn quite a bit if you give an examination where the students have to make some observations and then draw some deductions.

Taking Your Test Yourself

I like to take the examination at the same time the student does. Of course, I have made it out and have an enormous advantage. If I can't do the examination in less than one-third of the time the students are given there is something seriously wrong. If I can't produce a good set of examination answers by the end of the hour, have them

all dittoed so that, as the student leaves the exam, he can pick up a key, there is something seriously wrong. Yet I have great difficulty convincing teachers that they ought to do this and I have a theory as to the reason. I don't believe I have ever done this without making a mistake in the key, nor have I ever given myself 100 on my own examination; but most of us are too embarrassed to let the students know we can't get 100 on our own examination.

Objective Exams

Most peoples' objections to objective examinations boil down to the fact that they have to commit themselves before they give the test as to what the answers are. Let me start off with an example of an examination from a very prestigious group of people. The question relates to solutions of calcium chloride, CaCl2, and oxalic acid, H2C2O4, which when mixed precipitate calcium oxalate, CaC2O4, and an equilibrium is established. The question is "Which of the following would you do to dissolve the precipitate of calcium oxalate?" Four possibilities are offered: a) add more calcium chloride solution; b) Add more sodium oxalate; c) Stir the mixture; d) Add sodium chloride. Which of those is the correct answer for dissolving calcium oxalate?

Writing objective examinations has some inherent dangers. All of the answers are supplied and the mistake here is that whoever wrote this examination did not add e) "none of the above." But as soon as you put down "none of the above" you can almost be certain that it is a possible answer even when the person who wrote the question did not think so. I have never picked up an objective examination without finding a question I thought was completely impossible to answer.

What should be done about examinations? Every objective examination is in serious danger because you have to commit yourself on the answer while you were thinking along one direc-

tion and the student probably will be thinking in another. Here is one more example of this particular fact. During the War I taught at the University of California, Berkeley, in a military program and after the examination had been given at the end of the course the Colonel in charge said "Incidentally, I want you and your staff to take this examination." So we all went down and took it. A few days later the Colonel saw me and he said with a very sly smile "You know only one of you and your staff got a hundred on that examination" and I said "That's right, it was I, wasn't it?" He said yes it was, and I said the only reason I got a hundred was that I knew what the examiner wanted put down and I put down a half-dozen wrong answers. The graduate students who were not quite as sophisticated were much more honest and put down the correct answers. Therefore. they were graded down. I wonder how many of the students had achieved the level of sophistication that they should have achieved in the sense that they really understood the question and thus put down the right answers but were marked wrong.

Essay Examinations

Everything I have said about objective exams applies with at least equal force to essay exams, which are graded by a professor with a particular expectation; if the student takes a different position the student may get clobbered whereas the person who should get clobbered—with his own questions—is the professor. Designing exams is a very difficult task. One of the principal differences between objective and nonobjective exams is that, with objective exams, you have to put in your time before the exam and with the essay type after the exam, but you don't save any time. In both cases you feel very frustrated after the exam because you have given these students this absolutely magnificent instruction and they have returned it to you so badly mangled. But there is the question as to who mangled what.

Grading Efficiency

Whenever we give an exam we should think in terms of efficiency and effectiveness. In large sections of the academic community we have a very inefficient examination marking system. I recently had a chance to visit another country-it could just as well have happened in this country—where I was told about the examination system, how many thousands of papers in chemistry were given this last year and how many professors read those papers. By doing a very simple bit of arithmetic I found out that if the professors had worked eight hours a day, six days a week for a whole month, which is the time they had, they could have spent three minutes on the average paper. Now how effective can you expect to be when you spend three minutes per paper on an essay type examination? This is being done in many parts of the world. Is this an effective way and might it not be better to investigate other ways of giving examinations?

One of the difficulties with education is that in our continual experimenting, educational experiments almost always "succeed." It is the only human endeavor where as far as I know almost no one writes a paper and says that he tried an education experiment and it failed. Sometimes the students are not cooperative and very often we change the experiment the next time around, but

we are always very encouraged by the initial results and then we modify the initial conditions a little. I am exaggerating—I am sure someone somewhere must have admitted that he failed, but I would suggest that we condition ourselves to a little more failure in our examination system and to a little less student failure in the examinations.

IUPAC in Ceylon

The International Union of Pure and Applied Chemistry is considering having an international working meeting on the design, production, and evaluation of examinations. The meeting is tentatively scheduled for Ceylon next summer. Many countries are actively engaged in re-examining their examinations and all of them should be. One of the reasons for suggesting that the meeting be held in Ceylon is that of all the countries I know about personally Ceylon has most imaginatively approached the examination problem. Perhaps, from this and similar meetings, exams designed to change curricula and educate (as well as test) students and teachers may originate.

If our educational systems really are examination oriented, perhaps we should spend more time inventing questions worth exploring and less time writing books which answer only the old questions.

(For sample examination questions see appendix V, p. 118)

Selected Examination Questions

Some Random Samples Submitted in Connection with the Conference

These are not chosen as examples of the best possible items, but as typical of the general level and variety of questions submitted by participants at the conference. Some are imaginative, some are pedestrian, some, no doubt, are incorrect. (See p. 100.)

Department of Examinations, Ceylon—General Certificate of Education (Ord. Level), **Chemistry I,** 45 minutes.

- 7. The production of yellow smoky flame by a clean gas burner probably indicates: i) too little air in the mixture, ii) too much air in the mixture, iii) too much soot in the incoming fuel mixture, iv) unburnt gas issuing from the burner.
- 11. Which one of the following will show the HIGH-EST pH value, when brought into contact with moist pH paper? i) water, ii) water shaken up with wood ash, iii) milk, iv) soda water
- 16. Which one of the following changes would IN-CREASE the molar concentration of the products in ANY chemical reaction? i) increasing the pressure, ii) increasing the temperature, iii) adding a catalyst, iv) increasing the molar concentration of the reactants.

39 and 40 refer to the following experiment. 3 sterilized flasks 1, 11 and 111 (closed with cotton wool) contain 50 ml sugar solutions of the SAME strength. To test the function of two kinds of bacteria (A, B) the bacteria were mixed with the sugar solutions as in the Table below. After 4 days in a warm room, the contents of the flasks were analyzed, and the observations recorded as in the Table below:

Observation after 4 days
Sugar + alcohol in solution
Sugar + alcohol + acid in solution
Only sugar in solution

- 39. Which one of the following would be MOST VALID, from the above evidence ONLY? i) bacteria A converts sugar into acid, ii) bacteria B converts sugar into acid, iii) bacteria B converts alcohol into acid, iv) none of the above is valid.
- 40. To improve the above experiment, which one of the following is the BEST procedure? i) Repeat the above experiment several times, ii) Observe the action of A on alcohol, iii) Observe the action of B on alcohol, iv) Observe the action of B on acid.

Chemistry II. Two hours. Answer eight questions (out of 10).

- 2. Name two compounds which contain essentially C, H, O atoms, found in a Ceylon home. Describe one chemical test on one of these compounds, that you could do safely in the home, which will suggest that the compound contains carbon.
- 3. With one chemical test for each pair, describe how you would distinguish between finely powdered (i) sodium chloride and ammonium chloride, (ii) lead and zinc. State what happens to both substances in each pair.
- 7. Two plates A_1 and A_2 of metal A (3 cm x 3 cm x l cm) were fastened together with a bolt of metal B (dia. 0.5

cm) as in the Figure given below. The combination was hung in a warm humid room for about three weeks. It was found that the intensity of corrosion attack was GREATER on the plates A_1 , A_2 , than on the bolt.

Which of the following combinations of metals could be expected to give the above observations?

A ₁ ,A ₂	Sn	Mg	Cu	Zn	Fe	Au	Pb
В	Ag	Zn	Pb	Fe	Cu	Sn	Mg

Had the combination been exposed, as in the Figure 2 given below, with plate A_2 supported on a table with a piece of wood, where on the visible parts of Plate A_1 , would you expect the corrosion attack to be most intense? Give one reason for your answer.

University of London—General Certificate of Education Examination, Ordinary level, Nuffield Science Teaching Project, Chemistry II, two hours. Answer four of seven in Section A, two of seven in Section B.

Section A.

A2. In this question you will be asked to refer to the following: A—Dry hydrogen chloride. B—A solution of hydrogen chloride in dry toluene. C—A solution of hydrogen chloride in water. D—Pure acetic acid. E—A solution of acetic acid in water. F—A solution of potassium hydroxide in water. The solutions are all of the same molarity.

a) State three of them which would not change the color of dry blue litmus paper (indicate your answer by writing the appropriate letters).

b) Which two of them would you expect to be the best conductors of electricity?

c) An excess of B was shaken with some of F. Two layers were formed and they were separated by means of a separating funnel. The aqueous layer, which was found to be acidic, was evaporated and yielded a white solid (G). i) Name G. ii) Explain concisely the changes which take place when excess of B is shaken with F. Give appropriate equations.

d) Bronsted defined an acid as a proton (hydrogen ion) donor, and a base as a proton acceptor. Explain these definitions concisely by referring to the changes which take place when B is shaken with water.

A6. A solution of potassium auricyanide was electrolysed using a gold anode and a gold cathode. During the electrolysis gold was deposited on the cathode. The electrodes were weighed before and after the experiment.

	Cathode	Anode
Initial weight	25.104g	24.614g
Final weight	25.596g	24.122g
Current flowing 0.20 amp		
Time of current flow 60 minutes		

 a) Calculate the amount of electricity which flowed during the experiment. Give your answer in amp hours or coulombs.

A6. b) What weight of gold would have been deposited by 1 faraday of electricity (1 faraday = 26.75 amp hours or 96,540 coulombs)?

c) The atomic weight of gold is 197. How many faradays of electricity are required to deposit 1 g-atom of gold?

d) What does this experiment tell us about the number and kind of charges on one gold ion?

e) On the basis of these results a pupil wrote the following conclusions. Which of these conclusions do you consider (i) justified from the results (ii) not justified from the results?

A—Potassium auricyanide is a compound containing potassium and gold only.

B—Potassium auricyanide consists of molecules which change into ions when they are dissolved in water.

C—For every atom of the gold anode which changes into an ion, an atom of gold is deposited on the cathode.

D—Water is a good conductor of electricity.

E—Gold electrodes are essential for the electrolysis of a solution of potassium auricyanide in water.

F—The formula of a chloride of gold is likely to be AuCl₃.

Indicate your answer by giving the appropriate letter for each conclusion—i) Conclusions justified from the results, and ii) Conclusions not justified from the results.

Section B.

B4. Describe a simple fuel cell which uses hydrogen and oxygen as fuel. You should describe the apparatus, state the reactions which give rise to the electricity, and give reasons why scientists and engineers consider that work leading to the development of a fuel cell for use in industry is worthwhile.

B5. Describe three experiments which seem to you to indicate that matter is composed of small particles and that these particles are in motion. Describe what you would do, the observations you would expect, and how the observations lead to your conclusions.

B7. Magnesium carbonate reacts with hydrochloric acid according to the following equation:

MgCO₃ + 2HCl → MgCl₂ + CO₂ + H₂O Suppose you were given an impure sample of magnesium carbonate in which the impurities did not evolve gases when treated with hydrochloric acid. Describe how you would find the percentage of magnesium carbonate in the impure sample by using the reaction given above, and measuring the volume of carbon dioxide formed. Give full experimental details and indicate how you would calculate your answer.

. . .

Nuffield Chemistry Project. 1 hour 45 minutes. Answer all questions in Section A, two out of four in Section B, and two out of six in Section C.

Section A.

- 1. Three elements in Group I of the Periodic Table are sodium, potassium, rubidium. Sodium has the smallest atomic weight and is nearest to the top of the group; rubidium has the greatest atomic weight and is nearest to the bottom of the group. Which one of the three would you expect to react most vigorously with water? A—Sodium; B—Potassium; C—Rubidium.
- 3. Each of the following substances was heated in air until no further change took place. Only one of them contained carbon; which one was it? A—This substance was pink. It gained in weight and left a black residue. B—This substance was black. Its weight and color remained unaltered. C—This substance was black. It lost weight and formed a gas which turned limewater milky.

Section B

2. Imagine that you were shown the following five samples of sulphur. A—Rhombic sulphur; B—Molten sulphur just above its melting point; C—Molten sulphur just below its boiling point; D—Sulphur vapor above its boiling point; E—Plastic sulphur. i) Which one of these is crystalline? ii) Which one of these on cooling rapidly, would form monoclinic sulphur? iii) In which one of these are the molecules of sulphur at the greatest distance apart? iv) Which is the only one of them which would not change if reduced to a temperature of 0°C for some time? v) How could you tell which was B and which was C if an instrument for measuring temperature was not available? vi) Describe briefly how you would convert A into E.

In this conversion would you expect to obtain more, the same, or less, weight of plastic sulphur than the

weight of rhombic sulphur with which you started? Why?

3. A small, open tube containing 0.2 ml of liquid bromine was put onto a greased plate and covered with a iar of 5,000 ml capacity. The bromine weighed 0.64 g. In a few minutes the bromine had evaporated and filled the jar uniformly with its orange-coloured vapor. i) What is the weight of 1 ml of liquid bromine? ii) What is the average weight of bromine in each ml of air after it has completely dispersed? iii) Which one of the following is the least likely explanation of the fact that the bromine disperses throughout the jar? A-There is a lot of space between the molecules of air. B-Bromine molecules are lighter than air molecules. C-Bromine molecules are moving. iv) If the bromine had been released in the same jar from which most of the air had been pumped, which one of the following would have happened? A-The time taken to fill the jar with vapor would have been longer. B-The time taken to fill the jar with vapor would have been shorter. C-The time taken to fill the jar with vapor would have been the same. v) Suppose the first experiment had been repeated at a temperature of 20°C lower. Which one of the following would have happened? A-The time taken to fill the jar with vapor would have been longer. B-The time taken to fill the jar with vapor would have been shorter. C-The time taken to fill the iar with vapor would have been the same. vi) State briefly why you chose your answer to (v). vii) If the experiment is repeated using a piece of dry ice (solid carbon dioxide) instead of the bromine, the dry ice disappears but there is no apparent change in the air in the jar. Why is there no apparent change in the air in the jar? How would you demonstrate by experiment that the solid carbon dioxide had behaved in a similar way to the liquid bromine?

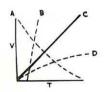
Section C.

- 3. Suppose you wanted to explain to someone who knew little chemistry that some chemical reactions can go both ways (they are reversible). Describe an experiment which would illustrate to him what is meant by a reversible reaction. The evidence on which your conclusions are based should be given clearly and simply.
- 4. It has been said that two substances are necessary for acidity to be displayed. What is meant by this statement? Imagine someone had been away when this was discussed in class. Briefly outline an experiment and its results, and explain to them how the facts support the statement.

Italy. Pilot course for the teaching of chemistry. One bour 45 minutes.

- 3. Is there more oxygen in the air you breathe on the Naples beach or in the air you breathe on the top of Vesuvius?
- 5. Air and nitrogen oxide are two colorless gases sparingly soluble in water. Two vessels are filled with these gases; how may you identify these gases?
- 10. Some magnesium powder is transferred into a glass vessel, closed with a stopcock. After some time the powder lost its brightness and became whitish. a) What reaction took place? b) How would you measure a pressure change inside the vessel? c) Do you think that a pressure variation might be observed inside the vessel if the stopcock was open?

U. S. High School-Better Students.



V-Volume

T-Absolute temperature

- 1. Which line represents the change of a gas if the gas is allowed to escape as the temperature is increased?
- 1-A, 2-B, 3-C, 4-D, 5-None of the lines.
- 2. Which one of the lines on the graph represents the ideal behavior of gases? 1—A, 2—B, 3—C, 4—D, 5—None of the lines.
- 3. Which line represents the change of a gas if the pressure on the gas is increased as the temperature is also being increased? 1—A, 2—B, 3—C, 4—D, 5—None of the lines.
- 4. The per cent of oxygen in Ca(OH) $_2$ is approximately (atomic weights: Ca=40, O=16, H=1) 1—16/74 \times 100, 2—16/57 \times 100, 3—32/74 \times 100, 4—16/58 \times 100, 5—None of the above.
- 5. Which one of the following accurately defines an element? 1—The smallest particle of a substance. 2—Cannot be decomposed into simpler substances. 3—Has variable composition. 4—The particles are associated but retain their individual properties. 5—A

substance which can be decomposed into simpler substances.

6. A volume of 500 ml of oxygen was collected at 273°C and 400 mm of Hg. What volume would this gas occupy if the temperature changes to 0°C, the pressure changes to 200 mm of Hg, and one-half of the gas is allowed to escape? 1—31.25 ml, 2—125 ml, 3—250 ml, 4—500 ml, 5—None of the above is correct.

U. S. TV Course-Chemical Equilibrium.

- 1. Put the number of the best answer in the parentheses.
- () In the reaction $A + BX \rightarrow AX + B$ (1) A is more active than B (2) X is an oxidizing agent (3) B is a reducing agent (4) there is no change in the oxidation number of any of the elements.
- 2. () One of the following reactions will not form hydrogen: (1) the action of steam on hot carbon (2) the action of steam on hot magnesium (3) the action of hydrochloric acid on hot silver (4) the action of cold water on sodium.
- 3. () One of the following type reactions will not form water: (1) Metal oxide + acid (2) Metal + acid (3) Metal hydroxide + acid (4) Metal hydroxide + acid oxide.
- 4. () If the oxide of an element reacts with acids to form salts, the element is (1) an acid (2) a metal (3) above hydrogen in the activity series (4) a non-metal.
- 5. () The molecular weight of a compound may be found by measuring any of the following except (1) the density of the vapor of the compound (2) the vapor pressure of the compound at known temperature (3) the vapor pressure of the solvent in equilibrium with a known solution of the compound (4) the freezing point of a known solution of the compound.

The University of the State of New York, The State Education Department, Special Examination in Chemistry, 3 hours, Part I answer all 60, Part II answer 4 of 6.

32. What conditions most favor a spontaneous chemical reaction? 1—decreasing energy content and decreasing entropy, 2—decreasing energy content and increasing entropy, 3—increasing energy content and increasing entropy, 4—increasing energy content and decreasing entropy.

33. Which carbonate is least soluble in water?

	Formula	Kap
(1)	BaCO ₃	5 × 10 ⁻⁹
(2)	CaCO ₃	4.8×10^{-9}
(3)	FeCO ₃	2×10^{-11}
(4)	PbCO ₃	1×10^{-13}

34. For the system $2A_{(g)} + B_{(g)} = 3C_{(g)}$, the expression for the equilibrium constant K is

(1)
$$\frac{[2A] [B]}{[3C]}$$
 (3) $\frac{[3C]}{[2A] [B]}$ (2) $\frac{[A]^2 [B]}{[C]^3}$ (4) $\frac{[C]^3}{[A]^2 [B]}$

35. Given

 $H_{2(g)} + 1/2 O_{2(g)} = H_2 O_{(g)} + 57.8 \text{ kcal.},$ the reaction is

- 1. exothermic, and the ΔH is negative
- 2. endothermic, and the ΔH is negative
- 3. exothermic, and the ΔH is positive
- 4. endothermic, and the ΔH is positive
- 36. What is the most logical value of the equilibrium constant K for a reaction in which the original reactants are largely converted to products?

(1) 1.0 (2) 0 (3) 10. (4) 1.0×10^{-4}

U. S. High School

1. For items.... through...., mark the pairs of factors according to the following key:

- I. An increase in the magnitude of the first will be accompanied by an increase in the magnitude of the second.
- II. An increase in the magnitude of the first will be accompanied by a decrease in the magnitude of the second.
- III. An increase or decrease in the magnitude of the first need not change the magnitude of the second.
 - 1. The temperature of a trapped mass of gas—The pressure of the gas.
 - 2. The concentration of salt in the undissolved phase of a salt-water system at equilibrium-The concentration of salt in the undissolved phase of this same salt-water.

U. S. High School (5 year, mostly college bound)

1. Given: the densities (in gm/cc) of the indicated metals:

antimony 6.62 lead 11.34 aluminum 2.70 bismuth 9.67 magnesium 1.74 nickel 8.60

Experimental results: I. When a mixture of lead and antimony is added to liquid J, only the antimony floats on the surface of the liquid. II. Addition of liquid K to a mixture of aluminum and magnesium results in the separation of the two metals, one floating on the surface of the liquid K and the other remaining on the bottom of the container. III. A mixture of antimony and magnesium is added to liquid L. The antimony sinks to the bottom of the container and the magnesium floats on the surface of the liquid L. IV. When liquid L is added to liquid K, liquid K floats on the surface of liquid L.

The liquids arranged in order of decreasing density are:

(1)
$$J > K > L$$
 (3) $K > L > J$ (5) $J > L > K$ (2) $L > K > J > L$

- 2. A certain colored but clear liquid called jexon has a density of 0.924 g/ml. When a sample of this material is distilled completely, no residue is left in the distilling flask. A sample of the material after distillation is found to have a density of 0.924 g/ml. Which term below best describes the nature of jexon?
- (1) pure substance, (2) solution, (3) chemical element.
- (4) mixture, (5) no conclusion possible.
- 2. A chemist removed two bottles from the laboratory shelf. One contained a gray, crystalline powder; the other a yellow crystalline powder. All of the yellow crystals appear to be the same, but different from the gray crystals. Upon heating, the yellow powder evaporated entirely at about 450°C. When he condensed some of the vapor on a cold surface, yellow crystals resembling those of the original yellow substance were obtained. The density and melting point of the condensed material were identical with those of the original yellow powder.

After mixing together some of the gray powder with a large amount of the yellow powder, the chemist heated them for half an hour. When the resultant material had cooled it was found to be a colorless crystalline substance which resembled neither of the original substances. The chemist then made additional studies and tabulated his results in the table of properties on p. 123:

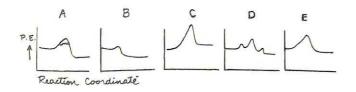
- 1. On the basis of the observations given there, the most precise conclusion the chemist can reach regarding the original gray powder is that it—(1) is an element, (2) is a compound, (3) is a mixture, (4) is a pure substance, (5) could be any of these.
- 2. The most precise conclusion he can reach regarding the original yellow powder is that it—(1) is an element,

	Original Gray Powder	Original Yellow Powder	Resultant Crystals
Melting point (°C)	419.5	112.8	Sublimes at 1185°
Boiling point (°C)	907	444.6	Sublimes at 1185°
Density	7.14 g/cc	2.0 g/cc	4.1 g/cc
Solubility in water	Insoluble	Insoluble	Insoluble
Solubility in HCl	Dissolves with evolution of colorless odorless gas	Insoluble 5,	Soluble, with evolution of colorless gas having foul odor.

- (2) is a compound, (3) is a mixture, (4) is a pure substance, (5) could be any of these.
- 3. The most precise conclusion he can reach regarding the resultant colorless crystals is that they—(1) are an element, (2) are a compound, (3) are a mixture, (4) are a pure substance, (5) could be any of these.
- 4. Heating the mixture of the original gray powder and yellow powder can be most precisely described as resulting in—(1) a physical change, (2) a chemical change, (3) decomposition, (4) transmutation, (5) a nuclear reaction.
- 5. The observations which most strongly support the conclusion in question No. 4 (regarding the effect of heating a mixture of the original gray powder and yellow powder) are those involving—(1) appearance and boiling points, (2) solubilities in water, (3) solubilities in HCl.

U. S. High School

1. Questions 1 to 6 have to do with the following curves. For each question choose the letter of the curve and place it in the proper place of the answer sheet.



- 1. Which of the curves represents an endothermic reaction?
- 2. Which of the curves represents a complex reaction mechanism?
- 3. Which of the above curves is most likely to be a self sustaining reaction?
- 4. Which curve represents a catalyzed reaction?
- 5. Which of the curves is most likely spontaneous?
- 6. Which of the curves represents the most stable reactants.
- 2. In the curve D for problems 1-6 which of the following equations would probably best fit the curve.

A.
$$A + B + C \rightarrow WX + Y$$

B.
$$A + B + C \rightarrow WXY \rightarrow WX + Y$$

C.
$$A + B + C \rightarrow AB + C \rightarrow WX + Y$$

D.
$$A + B + C \rightarrow A + CB \rightarrow WX + Y$$

E.
$$A + B + C \rightarrow AB + C \rightarrow WXY \rightarrow WX + Y$$

U. S. High School

Questions 1 and 2 refer to an experiment in which the solid copper is heated until melted.

3.11 kcal + $Cu_{(s)} \rightarrow Cu_{(1)}$ m.p. 1083°C The liquid copper is heated until it is changed into vapor.

72.8 kcal +
$$Cu_{(1)} \rightarrow Cu_{(g)}$$
 b.p. 2582°C

- 1. How much heat is required to melt 6.35 g of copper?
- 2. How much heat is required to vaporize 1 kilogram of copper?

A flask is half full of 1.00 M sodium carbonate, Na₂-CO₃, solution with solid water (ice) floating in the solution. The system has been standing long enough for equilibrium to have become established. The flask is stoppered. Use this information to answer questions 3-8.

3. How many phases are present in the entire system? List them. (Neglect the flask and stopper.)

- 4. Which of the phases present is a pure substance?
- 5. How many grams of Na₂CO₃ are dissolved in 500 ml of the 1.00 M solution?
- 6. The solution is heated until it begins to boil. The atmospheric pressure is 760 mm of Hg. Will the boiling temperature be: a) 100°C, b) higher than 100°C, c) lower than 100°C?
- 7. When $Na_2CO_{3(s)}$ dissolves in water, sodium ions, $NA^+(aq)$, and carbonate ions $CO_3^-(aq)$, are present in the solution. Write an equation to represent this reaction.

The West African Examinations Council General Certificate of Education, Advanced Level Chemistry. Section I—Answer all short-answer questions in 30 minutes. Section II—Answer 3 out of 5 on "General Principles." Section III—Answer 2 out of 4 on "Applications of Principles." Three hours total. (Specimen Questions)

Section I.

- 1. Radium (Ra) is a member of Group II of the periodic table (Be, Mg, Ca, Sr, Ba, Ra). On the basis of this relationship answer the following questions:
 - a. What is the physical state of radium at room temperature?
 - Give the chemical formulae of the possible oxides of radium.
 - c. Suggest the expected bond type in radium oxide.
 - d. Write the chemical equation for the reaction of radium oxide with water.
 - e. Write an equation for the effect of adding sulphuric acid to the aqueous solution obtained in part (d).
 - f. Would radium react with water at room temperature? If you answer yes, write an equation.
- 2. Which would you predict to be more soluble in water, 1-aminopentane or 1.4-diaminobutane? Explain your answer.

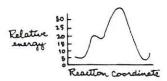
Section II.

8. The stoichiometric equation for the reaction of iodide ion with hydrogen peroxide in acidic solution is:

$$21^{-} + H_{2}O_{2} + 2H^{+} \rightarrow I_{2} + 2H_{2}O$$

a. Write the general form of the expression for the rate of appearance of molecular iodine.

- b. Can you predict the order of the reaction from the above equation? Justify your answer.
- c. If the initial concentration of hydrogen peroxide is doubled, iodine is formed twice as fast. What is the order of the reaction with respect to hydrogen peroxide?
- d. What would you expect to be the effect on the reaction rate if the concentration of acid were increased? Explain.
- e. If the reaction were started with 0.1 mole of peroxide and 0.5 mole of potassium iodide, how many moles of iodine would remain when the reaction was complete?
- f. Addition of one drop of ammonium molybdate solution causes the reaction to proceed at a much faster rate. Explain the possible function of ammonium molybdate.
- g. Assume that the reaction proceeds in two steps and can be represented by the following reaction profile.



Which step has the greater energy of activation? Which step is slower?

Section III.

13. a. The following equations represent the reactions of a solution of sodium hypochlorite which is sold as a bleaching agent.

OCI⁻ + 2I⁻ + 2H⁺
$$\rightarrow$$
 I₂ + Cl⁻ + H₂O
2OCI⁻ + 4H⁺ \rightarrow 2H₂O + Cl₂

Given two pint bottles of different commercial preparations outline how you would determine quantitatively which was the more effective bleaching agent. Indicate how you would prepare any solutions used in your analysis and specify the apparatus used.

- b. Write the ionic equation for the reduction of potassium permanganate under acid conditions. What volume of approximately 1 M sulphuric acid would represent a minimum volume of acid to use, in a titration using 25 cc pipettes, and 0.02 M potassium permanganate?
- c. Give full experimental details for the preparation of (i) 600 cc of 10% cane sugar solution, (ii) one liter of 1 M hydrochloric acid given that concentrated hydrochloric acid is 12 M.

MULTIPLE CHOICE: A NEW EXAMINATION METHOD

by H. Keri

Tradition has created two kinds of examination in Universities - oral and written. Both methods are highly subjective, and investigations are in progress all over the world to see which gives the better assessment of a student's knowledge in a short time. New methods are being elaborated in parallel with various testing procedures and programmed education.

The need for reform is not so pressing in secondary schools as it is in the universities. The number of lessons and the number of pupils in the class are determined by accepted, and decade-old, rules. Pupils are tested on many occasions so that chance and subjective factors play a lesser role in establishing the final mark. We do not wish to abolish certain subjective traits in marking, for if we did we should lose a considerable part of the educational effect of the mark. Neither an examination machine nor a teaching machine is a substitute for a teacher. On the other hand, the new methods have many advantages which make it worthwhile to use them alongside the traditional methods, and I wish to give an account of my own experience gained in work initiated by Szados Tamas at the Petrik Lajos Technical High School for Chemistry.

The Pupils There are 39 pupils in class I(a) in our school. At the end of the hear their average mark in chemistry was 3.1 - lower than expected. Their performance in the second half of the year was rather erratic. The class had an overall average of 3.6 and was one of the best in the school. Class I(b), with 41 pupils was one of the weakest. Its chemistry average of 3.1 was good compared with the overall average for the class. They have six lessons per week on general and organic chemistry and this considerable number makes it possible to treat the material in depth - at a level appropriate to the age of the pupils. There is certainly no need to have written tests just for the sake of collecting marks, and the method was used with a view to its other advantages.

Compiling the Questions This is a difficult task needing much circumspection. A feasible method is to staft a sentence and finish it with a number of alternatives, one of which is unambiguously correct and the others appearing probable to a certain extent. A combined cooperative effort is needed to produce a set of satisfactory questions. We can also get a lot of help from the literature. A series of questions can be selected from those that have already been tested and proven. I examined both classes twice using the multiple choice method, and I shall discuss the second examination in detail since it was given after the main chapters in the course had been gone over for a second time. The questions were adapted from Chemistry, a Basic Science, J.C. Hogg, D.E. Alley and CL. Bickel, Van Nostrand, 1957, with minor changes.

The Examination Pupils find this method strange at first. To begin with I allowed an hour for the purpose of familiarising them with the method. We solved similar questions orally, and practiced some calculations before the second test (the first test did not contain any calculations). This preliminary discussion aroused great interest and the pupils prepared themselves diligently for the test. Part of the preparation was to construct a grid on squared paper with question numbers 1 - 25 and 26 - 50 in vertical columns, and appropriate letters a, b, c, d, e in horizontal rows referring to the various alternative answers. The correct answer was indicated by marking a cross in the appropriate square. During the first test a number of pupils spent the entire time on the first question and did not even attempt to solve the last one. On the second occasion, however, they were able to go through the whole series. They were given 50 questions to answer in 50 minutes. Some finished ahead of time. I prepared a pre-cut pattern for assessing the test papers so that the number of correct answers could be quickly determined. We also agreed beforehand on the following mark scheme:-

up to	24 0	corre	ct answers	fails
11	31	11	П	passes
11	37	11	11	average
11	43	1.1	11	good
11	44 -	- ¹¹	II	excellent

The Questions A selection of 15 questions is given here by way of example. Correct answers are underlined.

3. Carbon dioxide

- (a) reacts with water to give a stable acid
- (b) reacts with water to give a strong acid
- (c) reacts with bases to give normal and acid salts
- (d) displaces air from a vessel with an inverted open mouth
- (e) is a product of photosynthesis

When water is electrolysed

- (a) the volume of oxygen liberated is double the volume of water used
- (b) the weight of hydrogen produced is double the weight of oxygen
- (c) hydrogen is liberated at the anode
- (d) oxygen is liberated at the anode
- (e) anode and cathode areas must be separated to prevent explosions

7. The only unambiguously correct equation among the following is:-

(a)
$$Hg + H_2SO_4 = HgSO_4 + H_2$$

(b)
$$Z_n + H_2SO_4 = Z_nSO_4 + H_2$$

(c)
$$3A1 + 2H_2SO_4 = Al_3(SO_4)_2 + H_2$$

(d)
$$A1 + H_2SO_4 = AISO_4 + H_2$$

(e)
$$Cu + H_2SO_4 = CuSO_4 + H_2$$

9. Hydrogen chloride

- (a) is a greenish-yellow gas
- (b) dissolves in water to give a strong acid
- (c) is a good conductor
- (d) is an unstable compound
- (e) can be produced by the action of dilute sulphuric acid on

17. Fluorine, chlorine, bromine and iodine constitute a family since

- (a) they have the same atomic weight
- (b) they have the same nucleus

- (c) they have the same atomic number
- (d) they have the same atomic structure
- (e) they have the same number of valency electrons
- 23. A molar solution contains a gram-molecular weight dissolved in
 - (a) a gram-molecular weight of water
 - (b) 1000ml water
 - (c) 1 litre of solution
 - (d) 1000 mol water
 - (e) 1000g water
- 24. In oxidation reduction reactions
 - (a) the valency of only one element changes
 - (b) the oxidising agent donates electrons
 - (c) the reducing agent accepts electrons
 - (d) every element undergoes a valency change
 - (e) the oxidising agent accepts electrons
- 25. A dilute solution of a strong acid
 - (a) is more ionised than a weak acid of the same concentration
 - (b) has a strong odour
 - (c) has a high positive charge
 - (d) has a very high concentration of acid molecules in the solution
 - (e) has a high negative charge
- 43. What volume of hydrogen at NTP is evolved when 4.9g sulphuric acid reacts with zinc according to the equation

$$Z_n + H_2SO_4 = Z_nSO_4 + H_2$$
 (H=1, O=16, S=32, Zn=65, 4)

- (a) 1.12 1, (b) 2.24 1, (c) 5.6 1, (d) 11.2 1, (e) 22.4 1,
- 44. According to the kinetic theory
 - (a) the density of solids is greater than that of gases
 - (b) three physical conditions exist
 - (c) the gas molecules are in constant motion
 - (d) the gas molecules are stationary
 - (e) kinetic energy cannot be transformed into other kinds of energy
- 46 . H=1, C1=35.5. 100ml solution contains 7.3g hydrogen chloride.

The normality of the solution is

(a) 0.1, (b) 0.2, (c) 1.0, (d) 2.0, (e) 10

I have tried to represent a variety of topics in selecting these examples. Some good questions and some not so good can be found. There was a high percentage of wrong answers in these selected questions and it is instructive to discuss the reasons for this.

Analysis of the Answers In question 3 pupils knew that (a) and (b) were not correct but a surprising number chose (d) and (e). Alternative (d) deliberately referred to an experiment which they had seen demonstrated but had not themselves performed. Our laboratory work is only loosely coordinated with the theoretical work. The considerable number of (e) versions indicated a further deficiency-lack of biology and biochemistry in the school curriculum. It was also apparent that I had not sufficiently stressed in our chemistry lessons that carbon dioxide is not a product of photosynthesis. There is a reasonable number of correct answers to question 6 considering the fact that the mistakes embodied in the incorrect alternatives are only evident after some thought. The correct answer to 7 was easily found. The equation was mentioned many times during the year.

The incorrect answers to 9 point in two directions. Some confused hydrogen chloride with chlorine. Others had not grasped the fact that concentrated sulphuric acid must be used to get hydrogen chloride from common salt. Question 25 revealed that many students were not familiar with the difference between a strong and a concentrated acid.

A few remarks on the calculation questions: question 23 is not, in essence, a calculation. It requires knowledge of an exact definition. Here again we find the usual mistakes. In question 43 we get few correct answers and incorrect ones distributed over each alternative. A possible explanation of this is lack of practice in solving problems quickly without using paper. Mistakes in question 46 were in the order number of pupils who are afraid to use their brains and do not even attempt to answer.

The Results In an approximately 50 minute interval I got answers from 40 pupils - i.e.approx. 2000 answers. These cover every aspect of the year's curriculum. Grading took less than 1 hour for the class. The important thing is that the results run parallel with marks obtained by the traditional method, whereas there are always considerable fluctuations in oral examinations. The fifty questions give us a realistic basis for judging individual pupils, and we can grade the entire class on a common basis.

VISUAL AIDS/AUXILIAIRES VISUELS



Teacher-Produced Instructional Films in Chemistry

A Note on the Use of Super 8 Film and Equipment for Original Production

The enthusiastic reception of the KODAK INSTAMATIC Movie Cameras has been due to the many very attractive features of these cameras — their compactness, small size and light weight, convenient and easy loading, automatic exposure control, motor drive, and other advantages. Among the satisfied users of this new equipment are many educators, audiovisual directors, and specialists who have realized its great potential for the making of motion pictures to be used in education at all levels. The cameras seem particularly suitable for the production of short single-concept films on a wide variety of subjects.

Contributing in no small measure to the acceptance of this equipment has been the adoption of the super 8 format and the excellent characteristics of KODACHROME II Movie Film, Type A. The high definition, excellent brightness, and full color saturation of the projected pictures have been so impressive that many people are envisioning a complete system with the super 8 film used as the camera film and numerous prints being made from this original.

There are some problems inherent in this idea, since the quality of prints made from a KODACHROME II original may fall short of acceptable standards. The material most commonly used for making prints from such originals is another reversal color film, somewhat similar in structure and processing requirements to KODACHROME II. This print film, designated EASTMAN Reversal Color Print Film, Type 7387, is intended for, and most extensively used for, the preparation of 16mm prints from low-contrast 16mm camera originals, such as EKTACHROME Commercial Film, Type 7255 (commonly used in 16mm professional motion picture work). The Type 7255 product is not, however, suitable for use in 8mm cameras and is therefore not available in the super 8 size.

When originals that have good projection contrast, such as films made on KODACHROME II, are printed on Type 7387, there is a substantial increase in contrast in the resulting print. A loss of detail in extreme highlights and deep shadows may result from this increased contrast. In addition, certain scene elements may be rendered darker than in the original and some hue shifts may occur. Whether such de-

partures in the reproduction are tolerable depends to a great extent on the particular subject matter, on the reflectance values of the scene elements, and, of course, on the lighting contrast used in photographing the original scene. From the standpoint of sharpness, the print may be very acceptable if the original footage is critically sharp and good contact between the original and the print film has been maintained during the printing operation.

For these reasons, you cannot expect that the print will be as high in quality as the original when you make a reversal super 8 contact print from a super 8 KODACHROME II original. Nevertheless, a number of people have felt that such prints serve a useful purpose and are often acceptable for the particular projects for which they were made. It is best in most cases to have a trial print made and then decide whether multiple print should be produced. If you follow this procedure, be sure that your decision is made before any damage to the original has occurred. Remember that scratches and imbedded dirt may result from repeated projections and these defects will reduce the quality of the print that is perhaps already marginal.

Another consideration is the matter of incorporating special optical effects — fades, dissolves, wipes, and so forth. At the present time, most laboratories do not have facilities for introducing such effects during the contact printing of super 8 originals. The finished print would therefore present only a straight scene-to-scene sequence without the embellishments seen in more professional productions.

It is hoped that future improvements in laboratory equipment and print material will provide solutions to these problems, thus making the super 8 system more amenable to a complete production system. However, such developments appear to be very unlikely in the near future. For the present, therefore, where it is known that multiple prints of high quality will definitely be required, the best approach is to plan the production for original photography on 16mm EKTA-CHROME Commercial Film and then have multiple reduction prints made by a commercial laboratory. A number of laboratories can now provide such service, using one of several established procedures.

The following suggested equipment list will provide all the basic items needed for an instructional film program in chemistry, with the exception of special apparatus which might be required for rarely-encountered needs such as microphotography. Special problems may best be handled by consulting major film and camera company representatives. All prices quoted are approximate only.

Equipment items actually used by the authors and found quite satisfactory are underlined.

Some representative brands of alternate equipment are listed. The authors do not imply that the equipment they used is the best available, but only that they recommend it as being satisfactory. No attempt is made to give an exhaustive equipment list or a "Consumer's Report" evaluation. Specific desirable features for each type of item are indicated and should be considered important, whatever brand of equipment is actually purchased.



1. EQUIPMENT FOR MAKING 8mm FILMS

Item	Approximate Cost	Desirable Features	Representative Examples
Camera \$150-\$300 Auxilary \$ 10-\$ 50		Through-the-lens viewfinder, zoom lens, single frame setting, variable filming speeds, automatic/manual exposure control.	H8 Rell and Hawell Autol
Auxilary Lenses	\$ 10-\$ 50	Must fit camera lens used. Should have at least $2+$ and $4+$ lenses. Consult camera dealer (a).	Tiffen lenses, Spiratone lenses, Vivator lenses, Ednalite lenses.
Lightmeter (b)	\$ 5-\$ 30	Available as either "incident" or "reflected" type. Latter often pre- ferred for closeup shots.	Kalimar auto-dial, Norwood su- per director, Yashica YEM-55.
Tripod Stand	\$ 15.\$ 60	Tilthead, panhead, medium weight, wobble-free.	Hollywood Jet General, Quick-Set Husky IV, Spiratone Heavy Duty.
Remote Cable Release	\$ 3.\$ 10	Must fit camera chosen; should be at least 18" long.	See local camera dealer.
Movie Lights	\$ 20-\$ 30 each	Should have three. Must have correct "temperature" for color balance (3400K), preferably quartziodine or quartz-bromine type bulb. Should have clamp for mounting on light stand.	Kodak Instamatic Movie Light— Model 2, Smith-Victor Q-1-P Movie Light.
Light Stands	\$ 10-\$ 25 each	Should have two or three. One light may be mounted with the camera.	PIC Light Stands.
Titling Sets	\$ 3.\$ 15	Preferably white or light colored letters for use on black background or black letters for light background.	Hernard Dimensional Letters, Press-Type Letters.
Film Editor	\$ 25-\$ 60	Should be tried in advance to see that picture is well lighted, film is not overheated, and there are no places where film scratching occurs. Specify 8mm or super 8.	8mm: Argus-Model 767, Mansfield Reporter-Editor 2008. Super 8: Argus-Model 768, Mansfield Reporter Super Eight Model 2080.
Splicer (c)	\$ 4-\$ 25	May use splicing tape or cement according to preference; should have spring fingers to hold film in place.	Kodak Presstape Universal Splicer (16, 8 or super 8), Victor Splicer VS-6 (16, 8 or super 8; cement or tape).

⁽a) For specific advice on lenses, see "Close-Up Movies," Kodak Pamphlet No. AD-30, free on request from Consumer Markets Division, Eastman Kodak, Rochester, N.Y. or free booklets on Vivator or Steinheil lenses from Ponder and Best, Inc., 11201 W. Pico Blvd., W. Los Angeles, Calif. 90004.

(b) Some of the newer cameras have only automatic exposure control, in which case no additional lightmeter is required.





SOURCES OF CHEMISTRY FILMS

In the past no concerted effort has been made to produce a carefully-edited catalogue of existing chemistry films with useful reviews. Hopefully such a catalogue will be available during the next year.

Film Directories

Index of Chemistry Films (Fourth Edition)
 Royal Institute of Chemistry

X To Joshin cochen es none coctatale (19,17) 30 Russell Square, London W.C.1, Eng. This index is the most comprehensive listing of films on chemical topics currently available. Approximately 1400 films and 400 filmstrips from more than 200 sources are included. The fourth edition lists films produced through September 1964. Designed for use by schools, technical colleges, universities and the training departments of industrial firms. this index includes offerings from the USA. United Kingdom and 20 other countries. It contains 127 film subject classifications and 77 film strip classifications and costs approximately \$1.10 prepaid.

Film Guide on Chemicals, Chemistry, and the Chemical Industry, 1965-66 Edition

Manufacturing Chemists' Association, Inc. 1825 Connecticut Avenue N.W. Washington, D. C. 20009

List contains 311 films from 100 sources covering many facets of chemistry, chemicals and the chemical industry, and suitable for many audiences including college students.

 United States Atomic Energy Commission 16 mm Film Catalog, Professional Level, 1965

Audio-Visual Branch Division of Public Information U.S. Atomic Energy Commission Washington, D. C. 20545

186 professional-level technical films are made abailable from ten domestic USAEC film libraries on a free loan basis for educational, non-profit, and non-commercial viewing. Listing includes title, date, time, sound, color, producer, sale and loan information plus a comprehensive paragraph summary of the subject content of the film. "Understanding the Atom Series", and the "1964 Geneva Film Series" are available from this source.

4. Argonne National Laboratory Catalogue of Motion Picture Films

Film Center, Bldg. 2 Argonne National Laboratory 9700 So. Cass Ave., Argonne, III. 60440 List contains 92 films produced by and for the Argonne National Laboratory covering topics ranging from the general nature of the Argonne Laboratory to specific experiments recorded for highly trained experts. Films are available on loan at no charge (other than return postage and insurance). Listing includes title, catalogue number, date, time, sound, and color information plus a paragraph summary of the subject content of the film.

5. Films on The Nuclear Sciences (1966 catalogue

National Science Film Library Canadian Film Institute 1762 Carling Avenue Ottawa, 13, Ontario, Canada

Summaries of 254 films are available from the Canadian National Science Film Library. Information is given on each film including country and production date. length, whether black and white or color, language versions available, producer and sponsor, technical or scientific adviser, description of content, and service charge or rental. The sections on general theory and principles, chemistry and metallurgy, and radiation and radioisotopes contain details on many films suitable for use in colleges and universities.

6. Bureau of Mines Films, 1965-1966

MOTION PICTURES

Bureau of Mines

4800 Forbes Ave., Pittsburgh, Pa. 15213 Tabulation includes information on 40 films with many relevant to the technological aspects of chemistry. These films are available from the Bureau of Mines without charge except for return postage. List includes information on film title, time, mailing weight, producer of the film, and a summary of the film content.

 Source Directory: Educational Single-Concept Films Available in Magi-Cartridges (Third edition, March 1966)

Commercial and Educational Division Technicolor Corporation

Box 517, Costa Mesa, California 92627 This is a current list of educational film producers and respective listings of single-concept films available in Magi-Cartridges for use in Technicolor Standard 8mm and Super-8 Instant Movie Projectors. It includes 66 titles on chemical topics available from seven sources.



Other Film Sources

Several series of films, film strips, and transparencies have been prepared for the chemistry classroom and are not completely reported in the directories just described. Most of these films have been prepared for beginning chemistry classes or for the in-service education of secondary school teachers.

Motion Pictures with Sound

Modern Learning Aids
 Division of Modern Talking Picture Service,
 Inc.

3 East 54th Street, New York, N. Y. 10022 This source offers 26 CHEM Study Chemistry Films (available in both 16mm and 8mm sound cartridge formats). In addition 11 films on chemistry laboratory techniques (available in 16mm), and three films titled "The Chemical Elements" (available in 16mm) are offered.

2. Coronet Films

Coronet Building, Chicago 1, Illinois Coronet offers the University of Akron Chemistry Laboratory Series (available in 16mm form), consisting of twenty-seven films and the Coronet Chemistry Films set (available in 16mm form), a series of twenty-one classroom films.

3. Encyclopedia Britannica Films, Inc. 1150 Wilmette Avenue Wilmette, Illinois 60091 The Chemistry on Film Series (available in 16mm form) consisting of one hundred sixty films is offered.

8mm Film Loops, Short Form, Silent 1. Advisory Council on College Chemistry

Teaching Aids Committee Film Project Chemistry Department, Stanford University Stanford, California Approximately 10 films have been produced at Oregon State University by W. H. Slabaugh illustrating what a chemist with ideas and a minimum of equipment can do to produce 8mm film loops designed for use in the college classroom. Approximately 10-single concept films have been made by J. A. Campbell by extracting relevant footage from CHEM Study films. Five single concept films have been made by S. A. Schrage by excerpt-

ing footage from existing films. These films are available only for examination and stimulation purposes at the present time.

- 2. United Nations Educational Scientific and Cultural Organization
 Pilot Project for Chemistry Teaching in Asia Division of Science Teaching, UNESCO Place de Fontenoy, Paris 7e, France Approximately 10 films, generally dealing with experimental topics treated in an "open-ended" manner have been made. Some emphasize the continuous variation methods developed in the Chemical Bond Approach.
- 3. The Nuffield Foundation
 Science Teaching Project
 Mary Ward House
 Tavistock Place, London S.C. 1
 Thirty-eight films have been prepared to
 supplement the new "O" level (secondary
 school) chemistry course development by
 Nuffield; this list includes loops on laboratory techniques, theoretical concepts based
 on experimental observations, measurement, industrial processes and uses of
 chemicals.
- 4. Association Films, Inc.
 600 Madison Ave.
 New York, N. Y. 10022
 Sixty-three chemistry films produced at Yale University are available with seven showing demonstrations on the preparation of oxygen, six showing demonstrations related to physical and chemical changes, and twenty-two on miscellaneous topics including laboratory techniques, basic principles, and structure.
- Genco Educational Films
 1800 Foster Ave., Chicago, Illinois 60640
 Five flms related to the detection and effects of nuclear radiation are offered.
- Encyclopedia Britannica Films, Inc. 425 North Michigan Avenue Chicago, Illinois 60611 Five films related to states of matter and properties of matter and eight describing laboratory techniques in chemistry are available.



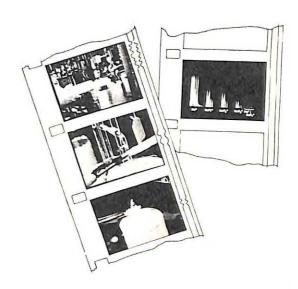
- Sutherland Educational Films
 201 N. Occidental Blvd.
 Los Angeles, California 90026
 Four films on some fundamental chemical concepts are listed.
- Gateway Educational Films Ltd. 470-472 Green Lanes Palmers Green, London N. 13, England Three films on paper chromatography, thinlayer chromatography, and electrophoresis are offered.
- Halas and Batchelor Cartoon Films, Ltd.
 Lysbeth House
 10A Soho Square
 London, W. 1, England
 Eight films on atomic and molecular structure are scheduled to be released in 1966.
- International Visuals Aids Center
 691 Chaussee de Mons
 Brussels 7, Belgium
 Sixteen films on technological topics related to chemistry have been made.

Transparency Sets

- John Colburn Associates, Inc.
 P.O. Box 1236
 1122 Central Ave.
 Wilmette, Illinois 60091
 Tecnifac Overhead Projecturals offer a general chemistry set of fifty-nine projectuals (with overlays) and a 48 page teacher's guide.
- Keuffel and Esser Company
 Hoboken, New Jersey
 Spectra transparencies for the overhead projector for chemistry are offered. This is a set of eighty transparencies (with overlays).
- General Aniline and Film Corporation 140 West 51st St. New York, New York 10020 Projecto Aid Transparencies consisting of a chemistry set of five transparancies are offered.

2 x 2 Inch Color Slides

- Geographical Slide Service 845 Outer Drive State College, Penna. 16801 Slides on minerals and manufacturing subjects are available.
- American Museum of Natural History Central Park West at 70th Street New York, N. Y. 10024 Slides on snow crystals, common rocks, and minerals are available.



Apparatus used in the preparation of xenon tetrafluoride with a photograph of the oscilloscope trace of the product identification in the mass spectrometer. Photographed from the color film "Xenon Tetrafluoride" produced by Argonne National Laboratories.

EQUIPMENT: ITS AVAILABILITY AND USES

Basic to the renewed interest in using film in the chemistry classroom and laboratory is the introduction by the industry of unproved film, film formats and complementing hardware. With these new developments comes an increased need for the chemistry teacher to understand not only the capabilities of the new hardware but also some of the important principles of projection. Included in this section is information on film formats, projectors and their characteristics, sound screens and some new developments in still projection techniques. The aim here is to provide a handy guide for the purchase and the setting up of equipment so that the best results can be obtained.

Film types. There are currently four forms of 8mm motion picture films on the market in addition to the traditional 16mm format. These are the regular 8mm, Super-8, Format M and a Japanese product. Of these the regular 8mm and the Super-8 have been used most extensively in teaching films.

The image area on the Super-8 film is 52 percent larger than that of the regular 8mm. Consequently the Super-8 format offers a brighter and sharper picture than that obtained from a



regular 8mm material under comparable conditions. Both regular 8mm and Super-8 can give magnetic sound prints with a quality comparable to present 16mm optical sound. Because the sprocket holes are smaller and further apart on Super-8 film than on regular 8mm film, each of the 8mm formats requires its own projectors and cameras. However, several manufacturers offer equipment which can be converted from regular to Super-8 with minor adjustments.

The running time of the 8mm films is approximately twice that of the 16mm. For example at silent speed (18 f.p.s.) 100 feet of 16mm film will run in about 4 minutes while only 50 feet of regular 8mm film will run in about the same time.

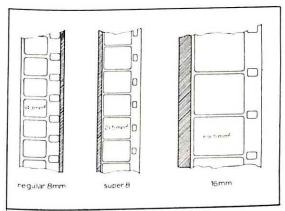
Projectors. Table F-6 gives some examples of film projectors, their important characteristics and manufacturers.

TABLE F-6

Typical Film Project	tors, Their C	Characteristics and Manufacturers	
8mm Front Screen Technicolor Model 500 (cartridge load silent).	Coct	Fairchild Mark IV (cartridge load sound)	Cost
Technicolor Corp., 1985 Placentia Ave., Costa Mesa, Calif. Fairchild Mark V (cartridge load	\$ 85.00	Super 8-mm, Rear Screen Not available as single unit; must be a combination unit; see page 29.	\$495.00
sound). Fairchild Camera and Instrument Corp., Industrial Products Division, 750 Bloomfield Ave., Clifton, N. J. Bolex 18-5, Auto load, silent Super-8mm, Front Screen	\$560.00 \$164.50	 16mm, Front Screen Bauer P-6 Auto load, quartz I₂ bulb magnetic and optical sound. Bell and Howell Auto load 552 Bell and Howell 302-M magnetic sound 	\$1250.00 \$755.00 \$950.00
Technicolor Model 510. (cartridge load, silent). Technicolor Corp., 1985 Placentia Ave., Costa Mesa, Calif.	0.00	 Graflex Model 815 manual threading RCA Safethreader No. 1600 Eastman Kodak AV105mm magnetic sound 	\$625.00 \$617.00
Eastman Kodak M-90 Reel load, silent. Eastman Kodak Co., Apparatus and Optical Div., 343 State St., Rochester, N. Y. Eastman Kodak M-100 Reel load, sound. Eastman Kodak Co., Apparatus and Optical Div., 343 State St., Roches	\$ 99.50 \$189.50	Special Purpose Projectors Magnetic Sound Technicolor Model 800 projector No. TMT - 25 telesell Kalart Soundstrip 35mm optical sound filmstrip. The Kalart Co. Inc. Hulls	\$995.00 \$670.00 \$270.00
Bauer T1-S, Quartz I ₂ bulb auto load, sound can be added by accessory	\$575.00 \$179.50	¹ Allied Impex Corp., 300 Park Ave., New York, N. Y. ² Bell and Howell Photo Sales Co., 7100 McCormick Rollinois ³ Graflex, Inc., 3750 McCormick Rollinois	d., Chicago,
Technicolor 600 console viewer (cart-	\$199.50	 RCA-Radio Corp. of America, Inc., Front and Cooper 15-5, Camden, N. J. Eastman Kodak, Rochester, New York Victor Animatograph Corp., Div. of Kalart, Hultenius ville, Conn. 	



8mm front (wall) screen projectors. The home variety of projectors which utilize regular 8mm film generally are not suitable for front screen projection in classrooms. The Bolex Model 18-5 (\$200.00) is an example of a high quality projector which has been used successfully for this purpose. Among the cartridge loading projectors, the Technicolor Model 500A offers an inexpensive regular 8mm projector (\$85.00) with still picture capabilities, without sound. This projector takes a four-minute cartridge. The manufacturer indicates that it will give a satisfactory 30" by 40" image in a darkened room on a wall screen. It has been used for front screen projection in small areas under carefully controlled conditions.



A comparison of regular 8mm, Super 8mm and 16mm film formats. The shaded areas indicate the space available for the sound tracks.

Super-8mm front screen projectors. Here the teacher has a choice of supporting models with improved light sources and lenses. The Eastman M-90, reel type (\$180) or the Bauer (\$179.50) are examples of Super-8mm projector design. The Eastman M-100 projector has magnetic sound capabilities, and, in operation, offers suitable performance in the small classroom. It is comparable in price to 16mm sound projectors. The Technicolor 510-A (\$90.00) is the only Super-8 cartridge load projector on the market at present. It has no sound capability and takes a four-minute cartridge.

16mm front screen projectors. Considerable improvements have been made in loading characteristics and light output of 16mm sound projectors in recent years. These improvements fa-

cilitate immediate classroom use of films and film segments. The simplified operation, and improved picture, will be of interest to those who have not examined the new models. Auto-loading characteristics are such that the inexperienced instructor or teaching assistant can get a picture on the screen in a matter of seconds with an absolute minimum of training. Examples of this equipment include:

Bell and Howell Autoload Model 552	\$	755.00
RCA Safethreader Model 1600 "Safethreader"	\$	617.00
Graflex Model 815 (manual loading projector)	\$	625.00
Bauer P-6 Autoload, incadescent or quartz I ₂ projection bulbs		
available	\$1	250.00

The following projectors offer a combination of optical and magnetic sound reproduction features. They also have a feature which permits the user to add his own sound track to the film (magnetic recording feature).

Bell and Howell Filmsound 302 M	\$950.00
Eastman Kodak Model AV-105M	\$885.00
Victor Mag-3	\$670.00



A Technicolor projector and film cartridge.



Sound conversion units are available to provide magnetic sound recording and playback capabilities for existing equipment. The Gregory Sound Conversion Unit sells for \$195.00 plus installation. For a discussion of magnetic and optical sound, see below.

8mm rear screen projectors. A self-contained rear screen and projector for 8mm film resembles a small television set. The advantage of rear screen projection is that it can be used in the normally lighted laboratory or classroom. Current model projectors take cartridged film. They are extremely simple to operate requiring a minimum of maintenance. The only projectors of this type now offered in the regular 8mm size, are the Technicolor Model 600AD (\$250.00) and the Fairchild Corporation Mark IV projector (\$495.00). The Technicolor projector uses a four minutes cartridge; the Fairchild projector takes a cartridge which holds up to 22 minutes of color film. Magnetic sound is a standard feature with the Fairchild projector. Color prints of the CHEM study films are available in cartridges for Fairchild projectors. One model of the projector is equipped with a magnetic recording feature (model IVAV).

16mm projectors for rear or front screens. The Kalart-Victor projectors use regular 16mm film in combination which provide both front and rear screen projection capabilities.



A Fairchild projector and film cartridge

Light sources. The General Electric Mark 300 high intensity light source, available in many new projectors, so increases illumination on the screen that film can be shown under normal classroom lighting conditions.

When considering the purchase of new projection equipment which might be used in a large lecture hall, suppliers should be given the room dimensions, lighting conditions and other features in addition to the projector capabilities desired. All such equipment should be tested in the rooms in which it will be used before a purchase is made.

Rear screen projection cabinets. Good commercial rear screen projection cabinets are available for use with a variety of projectors running from 35mm slide to 8mm and 16mm movies. The Hudson Photographic Industries 8mm screen (\$17.00) and the H. Wilson Corp. 16mm screens (\$150.00) are examples. For the the "do-it-your-selfer," the Eastman Kodak Pamphlet No. S-29 REAR PROJECTION CABINETS offers excellent directions on local fabrication.

Sound characteristics of film. Conventional 16mm sound film has an optical sound track in which the sound reproduction is stimulated by light. Films now can be supplied with magnetic sound tracks. Here the sound reproduction is stimulated by the interaction of a magnetized stripe on the film with a charged head in the projector. The magnetic sound stripe similar to that on an audio type can be added to film prior to photographing. Sound can be recorded as the film is exposed in the camera, or it can be added later using projector with a magnetic recording capability. Eastman film, Kodachrome II No. KA558, can be ordered now from dealers. A camera suitable for this use is discussed on page 31. Probably more important to the teacher is the fact that 8mm, Super-8 and 16mm film can be shot silent and the magnetic stripe added when the film is processed. This affords the opportunity of adding a sound track to the film as it is run through the projector. Magnetic striping makes it possible to add a second sound track to films with sound. Magnetic sound tracks can be erased and corrected as with an audio tape recorder.



TABLE F-7

No. of Prints Ordered	Size Negative Submitted	Total Cost per 8mm ft.	Addition of Sound Stripe	Addition of Sound from 16mm master tape
Regular-8	16mm			
or Super-8		34		
1		12-18¢	3-16¢	11-24¢
2-9		8-15¢	3-13¢	100000
25 up		6¢	8-9¢	3-11¢
Regular-8	Super-8		3	1-1-5
or Super-8	1.53			
1		17¢	NA	NA
2-9		17¢	NA	NA
10-24		NA	NA	NA
25-49		NA	NA	NA
16mm	16mm	Total Cost		(Only recommended
Tollilli	1011111	per 16mm ft.	181	source: Eastman
1		19-22¢		Kodak; write for
2.9		11-22¢		prices and
10-49		11-16⊄	7	details on Sono-
100 up		5.4¢ (With		track coatings)
100 up		Magnetic sound)		

Prices do not include costs of internegative, printing effects, prints from A and B rolls, minimum charges, or discounts to schools. Contact the laboratories for specifics.

TABLE F-8

Some Laboratories Offering 8mm Release Print Service				
The Calvin Company 1105 Truman Road Kansas City 6, Missouri	George W. Colburn Laboratory, Inc. 164 North Wacker Drive Chicago 6, Illinois	Hollywood Valley Film Laboratories 2704 West Olive Avenue Burbank, California		
Cine-Chrome Laboratories 4075 Transport Street Palo Alto, California 94030	De Luxe Laboratories, Inc. 850 Tenth Avenue New York 19, New York	Technicolor Motion Picture Corp 6311 Romaine Street Los Angeles 38, California		
Cine Magnetics, Inc. 202 East 44th Street New York 17, New York	General Film Laboratories Corp. 1546 N. Argyle Hollywood, California	Western Cine 312 So. Peal St. Denver, Colo. 80209		
nal for the bear of all de the se or adverse became all marche force or all of the second are another top	Hollywood Film Enterprises, Inc. 6060 Sunset Boulevard Los Angeles, California			



Inquiries concerning magnetic striping processes and costs should be directed to the film processors.

Film costs. For those planning to make their own films, Table F-7 gives approximate current costs for the printing of silent color films and for addition of magnetic sound stripes. Table F-8 lists some laboratories offering release print service.

Cost of cartridging films. Cartridge costs range from one to ten dollars (based upon the kind of projector and on the quality ordered). Technicolor Corporation now will furnish and load cartridges for their projectors at a cost of \$1.00 when suitable 8mm film is furnished. Cartridges for the Fairchild projectors cost from \$6.60 to \$9.95 and special film treatment for films longer than 200 feet is necessary at a minimum cost of \$4.00. Those desiring to have films put in cartridges are encouraged to contact the Technicolor or Fairchild Corporations directly.

Cameras and lenses. Accompanying the introduction of the new film formats and projectors are improved cameras. Cartridge loading of cameras with Super-8 film is simplified since the cartridge need not be turned when half the footage film has been exposed. Zoom lenses permit going from a wide picture to a close-up and vice-versa without stopping or moving the camera. Reflex cameras with "through-the-lens" capability allow precision composing and focusing of close-ups. For photographing close-ups of laboratory equiment or reactions, cameras with a retail price of \$75.00 or less probably will not give acceptable steady picture quality.

Two professional cameras which are available for 8mm film are the Bolex H-8 (\$480.00), and the Pathe DS-8 (\$900). The latter is the first camera to use a 100 foot double Super-8 film spool. The Fairchild Model 900 (\$900) is now on the market as a regular 8mm sound motion picture camera.

Plastic lenses are excellent for some uses; however, experience has shown that glass lenses are more suitable in close-ups for chemistry uses. Cameras with fast lenses (aperture not greater than f/1.9 and able to accept accessory close-up lenses are a necessity for quality film makeup. Slower lenses restrict camera use in

the usual low light situations encountered in the laboratory.

Still projection systems. Several new still projection systems which have appeared recently are described in the following paragraphs.

Filmstrip with magnetic sound. The Execugraf (\$375.00) uses a film and a sound cartridge: the film cartridge contains up to one hundred 35mm pictures, and the continuous loop sound tape cartridge has a running time up to twenty minutes. This projector has both the front and rear view facility.

Filmstrip with optical sound. The Kalart Sound strip projector (\$400.00) uses a continuous strip of film identical with a sound movie except that the picture and the accompanying sound track are printed on alternate frames. Pictures, or slides with accompanying narration on audio tape can be sent to the manufacturer for conversion to this format.

Slides with sound. The Hughes Video-Sonic (automatic control) projector Model 901 (\$400.00) is a self contained rear screen projector which accepts 35mm slides in 36-slide trays. It has magnetic tape for audio.

Audio attachments for slide projectors. In many cases it is possible to use existing equipment, or combinations of projectors and recorders, to generate automatic presentations of slides and sound. The Kodak Carousel Sound Synchronizer (\$20.00) enables the instructor to combine a stereo tape recorder of any type with a Carousel Model 700 or Model 800 projector. Slide-change signals are recorded on one channel and the narrative on the other track. On playback, slides change automatically; this system is easy to connect and use.

A synchronized sound-film system. This is available for the Technicolor Model 800 Projecjector, from Ealing Films or Auto-Sell, Inc. (\$255.00 for projector and recorder). Both tape and film automatically stop when the end of the film loop is reached. It is possible to program the film loop for double or triple showing, using up to 20 minutes of narration.

Special effects. The Kodak motion adapter unit (\$24.00) consists of a spinning polarizer which fastens on the front of any 35mm projector lense and requires especially made slides which



contain elements of polarizing material. An effective motion illusion is possible including continuous or cyclic movement, rotation, vibration, and radiation. Technical Animations, Inc. can prepare motion slides on a custom basis. The American Book Company will be the distributor for motion slide series. Eastman Kodak, Audio-Visual dealers, will handle orders for slides. Experimental kits of Technical Animation polarizing materials are also available from the dealers. Prototype slides showing vibration modes of molecules now are available.

Random access slide projector. One of the disadvantages in using slides to augment lectures has been that the lecturer is tied to an order of projection not easily changed. This disadvantage is overcome with the appearance on the market of random-access, 35mm automatic slide projectors, such as the Dial-A-Slide projector (\$700.00) or Eastman Kodak RA-950 projector (\$785.00). Both projectors have controls which tell the instructor which slide is being projected. Similar units are available for connection to data retrieval systems.

UTILIZATION OF PROJECTED MATERIALS

Regardless of the quality of a motion picture film or slide, or the advanced state of the art in hardware, successful projection techniques remain the key to transferring ideas and concepts from the projected image to the students' mind. By following good practices in setting up a classroom or laboratory for the showing of film, the instructor gains the ultimate flexibility for utilizing a slide or film clip in the lecture with the confidence that the class will receive the maximum benefit from the medium.

This section is intended to help clarify some of the steps necessary to insure that the message reaches the class without interference by the projection process.

For effective projection in the classroom, consideration should be given to the following:

- selection of a screen location, size, and type.
- selection of the optimum projector location.
- providing required image brightness.

 general considerations of student comfort in the lecture room including light control, adequate sound facilities, and seating.

For the optimum use of projection during a lecture there should be a minimum of equipment and facility adjustments. For all practical purposes, the screen should be in a fixed position away from direct light sources and from areas used more frequently, e.g., avoid if possible a screen location where a roll-down screen covers the chalkboard.

Under ideal conditions, the instructor should be able to push a button and insert into the lecture a film or slide for seconds or minutes as needed, with absolutely no mechanical distractions to the class.

Projection screens.° The screen is most often the weakest link in using the projection systems. The efficiency with which the screen can transmit color brightness and contrast to the eye, affects the ease with which the point being made can be understood by the student. Following are brief discussions of screen types and their suitability to classroom or laboratory applications:

Matte screens. Matte screens diffuse light evenly in all directions. Images on matte screens appear almost equally bright at any viewing angle. To avoid distortion because of viewing angle, however, viewers should be no more than about 30 degrees to the side of the projection axis, and not closer than two-image widths to the screen.

Most matte screens are about 85% efficient. A metal finish matte screen will give valuable color correction to pictures where true rendition is important. A form of matte screen can be a smooth wall painted white, although it should be viewed critically before accepting it for classroom use.

Lenticular screens. These screens have a regular pattern of stripes, ribs, rectangles, or diamond shaped areas. The pattern is too small to see at viewing distances for which the screen is designed. The screen surface may appear to be enameled, pearlescent, granular metal, or smooth metal.

^{*}Most of the information on screens was taken from Eastman-Kodak publications.



By control of the shape of the reflecting surfaces, the screen can reflect nearly all the light from the projector evenly over a fan shaped area 70 degrees wide and 20 degrees high. Many lenticular screens provide an image three or four times as bright as a matte screen.

Beaded screens. Beaded screens are useful in long narrow rooms or other locations where most viewers are near the projector beam. They are white surfaces with imbedded or attached small clear glass beads on silica chips. Most of the light reaching the beads is reflected back towards its source. Thus, a beaded screen provides a very bright image for viewers seated near the projector beam. As a viewer moves away from the beam, the image brightness decreases. At about 22 degrees from the projector beam, the image brightness on a beaded screen will be about the same as that on a matte screen. Beyond this angle it will be less bright than on the matte screen. Students should sit no closer than two and one half times the image width from a beaded screen.

Rear-projection Rear-projection pictures have the same requirements for image brightness, size, and contrast as front-projected images. Rear projector screens are made of glass, plexiglass, or flexible plastics with one side of the screen a matte surface.

To reduce space requirements in rear projection, short focal length lenses sometimes are used. A single mirror between the projector and the rear screen is necessary; however large mirrors must be avoided. A special lens with a mirror encased and suitable for this purpose is avilable from Buhl Optics.

With most projectors, images as wide as 42 or 48 inches will be satisfactory on a dark rear projection screen in moderately lighted rooms. For larger images, a light screen in a darkened room is usually needed. In very brightly lighted rooms, images should usually be no more than 24 or 30 inches wide and the screen material dark.

Front vs. Rear Projection. In considering which projection system is best for given conditions, two common arguments regarding both systems are discussed below.

Shortened projection distances are claimed as an advantage by proponents of each system. While this is true in both cases, a short projection distance often does not give the image sharpness and brightness desired. However, when space is at a premium, short projection distances may be necessary and the equipment can be made to perform adequately.

Visibility in lighted areas also is claimed as an advantage by proponents of both front and rear projection. Either system will do a good job, depending upon conditions. When a small image (up to 3 feet wide) is desired, a dark colored rear-projection screen may provide dramatically better image contrast and color saturation than a front-projection screen. Although a rear-projection screen reduces image brightness, the amount of room light reflected toward the audience is reduced by an even greater factor. The back of the screen must be shielded from stray light. Front-projection screens always must be shielded from direct light.

When a large image (wider than 3 feet) is desirable, front-projection systems using a lenticular screen usually give better results than rear-screen systems. Location and control of room lights are important factors to consider here. In any case, more care must be given to the orientation of the projector, screen, and audience than is necessary for a smaller rear-projected image.

Screen Size. This should be such that the back row of viewers is no more than six times the image width (W) from the screen, with the following exceptions:

a. Certain materials, including many teaching films, are designed with titles and important picture elements bold enough to permit satisfactory viewing at distances of 8 to 10 times the image width. When this is true for the materials to be projected, the projector may be moved closer to the screen to give a smaller and brighter image. Moving the projector enough closer to change the back row from 6W to 8W will approximately double the image brightness and allow the front row to be moved a little nearer the screen.



b. In some situations, materials which limit maximum viewing distance to less than 6W are commonly used. Typewritten material projected with an overhead projector is an example. For showing the full area of an 8.5 by 11-inch page, pica type calls for a maximum viewing distance of 3W. The teacher should *critically* test this for his particular situation, perhaps by taking the poorest seat in the classroom.

A discussion of screen size with excellent solutions to common puzzles is available in Eastman Kodak publication *Effective Slides* S-22, and *Legibility Standards for Projected Material*, S-4, and in the ACS publication, *How to Make Slides*.

Image brightness. Required brightness (the amount of light the student sees) depends on viewing angle; screen type; projector design, wattage, life rating, and age of lamp; character of material being projected; image size; line voltage; as well as on the design and cleanness of the optics. Lamp wattage alone gives little indication of image brightness. Using wattage as a measure of image brightness is comparable to rating an engine by the fuel consumed rather than the work done.

The effectiveness of a projector, expressed as image brightness, is defined in terms of lumen output. Lumen output divided by image area (in square feet) gives the foot-candles falling on the

screen from the projector. Foot-candles of illumination multiplied by the reflectance of the screen (about 0.85 for a good matte screen) gives in foot-lamberts, a measure of the brightness of the image seen by the viewer.

Thus, a projector with a 120-lumen output provides 10-foot-candles of illumination for a 3 by 4-foot (12 square foot) screen image; that is, 8.5 foot lamberts of image brightness for the viewer of a good matte screen. With a projector light output of 80-100 lumens, and a matte screen in a well-darkened room, an image 3 or 4 feet wide can be viewed easily. As a rough estimate of the image brightness required, there should be as many foot lamberts of light per square foot of screen as there are foot candles of light in the room. For a more detailed discussion of image brightness see Eastman-Kodak publica-"What Can You Do With 100 tion S-14 Lumens?"

Projector location. Optimum projector locations depend upon a variety of factors including the lens and the screen size. Most manufacturers of projectors as well as lens suppliers (Buhl Optical Company) can provide a wide range of lenses for any type of projector. To decide on the lens needed for a given projector and situation, one should first determine the size of the screen to be used and then with the aid of a table such as Table F-9, the correct focal length for the lens can be calculated.

TABLE F-9

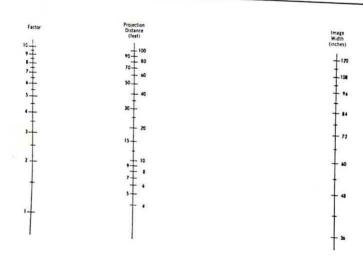
Determining Projection Distance, Image Width, or Lens Focal Length*

To determine the projection distance for a desired image width (or the image width for a desired projection distance), find in the following table the factor that applies to the film format and lens you are using. Then position a straightedge on the nomograph so that the edge passes through the points for the two known figures; read the third figure at the point where the edge passes through the other scale. For greater accuracy, add the focal length of the lens to the projection distance determined for a desired image or subtract the focal length from the desired projection distance when determining the image width.

To determine the best lens focal length, position the straightedge so that it passes through the desired image width and projection distance. Now read the figure that is nearest to the point where the edge passes through the left-hand ("Factor") scale and then consult the table to find the lens with the factor nearest to this figure. If screen size is a limiting element in the projection situation, choose the lens with the next larger factor.



Type of Material	Lens Focal Length (inches)	Factor	Type of Material	Lens Focal Length (inches)	Factor
16mm Motion Pictures (0.284" x 0.38" projector mask)	1½ 15% 2 2½ 3	3.9 4.2 5.3 6.6 7.9 10.5	4.2 5.3 6.6 7.9 10.5 2 × 2" Slides (38mm square or 26.2 × 38mm horizontal mask) 5.2 7 - 6.0 2 × 2" Slides (26.5mm square mask) (KODAK INSTAMATIC)	3 4 5 7 9	2.0 2.7 3.3 4.7 6.0
Super 8 Motion Pictures (0.158" x 0.211" projector mask)	1.1 (28mm) Zoom (20 - 32mm)	5.2 3.7 - 6.0		Zoom (4 · 6)	7.4 2.7 · 4.0
8mm Motion Pictures (0.129" x 0.172" projector mask)	3/4 % (22mm) Zoom (15 - 25mm)	5.0 3.4 · 5.7		4 5 7 9 11 Zoom	3.8 4.8 6.7 8.7 10.5
Filmstrip (17.2 x 23.0mm) projected area)	4 5 7	3.3 4.4 5.5 7.7	4.4 5.5 7.7 Lantern Slides (Mask opening 3" wide) 3.0 3.7 Overhead and Opaque (Material 10" wide)	(4 - 6) 6½ 12	3.8 - 5.7 2.2 4.0
2 x 2" Slides (23 x 34mm horizontal mask)	3 4	2.3		16 26	5.3 8.7
	5 7 9 11 Zoom (4 - 6)	5.2 6.7 8.2		14 18	1.5 1.9



^{*}Reproduced through permission of Eastman Kodak.

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Microchemistry Projected (TOPS)

Projection of micro-experiments is a new technique which involves each student in laboratory work, yet fits the budget of every classroom in the world. Grams are used instead of kilograms; an entire year of experiments costs five dollars. Chemical reactions are projected in full color on the wall; beakers appear a meter high; bubbles of gas and droplets of liquid appear as big as baseballs; noxious gases, smokes, and explosions are of micro-dimensions. Apparatus is immediately ready to use or to lay away. In fact, experiments using the UNICELL described below could be carried out individually by 1000 students in a lecture hall. This article describes the technique, summarizing a monthly series which has appeared in This Journal since 1962. It includes the following information.

(1) Chemicals: Sixty-one reagents; the dangerous ones have been omitted. (2) The UNICELL: a simple apparatus used for performing several hundred experiments. (3) Picture-book experiments: nine demonstrations illustrating the versatility of the UNICELL. (4) Student Workbook: questions to be answered and research

proposals to be suggested by the student during a single experiment; the displacement of Cu^{2+} by Fe is used as an example. (5) Teacher Manual: General instructions to the teacher; special instructions for the $Cu^{2+} + Fe$ experiment; answers expected from the student. (6) Projectors: two homemade projectors; details for making an inexpensive (\$0.50) lensless projector; commercial projectors.

Chemicals

Of the chemicals listed in the TOPS series² the following suffice for the beginning teacher. Dangerous chemicals such as concentrated acids or flammable substances have been omitted. The original numbering system in the TOPS series has been retained in the list below. Store the reagents in 50-ml square glass or plastic bottles.

Liquids

1. CH ₃ COOH (vinegar)	28. Hg
3. AlCl ₃ (aq)	30. Methylene blue (aq)
4. NH ₄ OH	33. NiCl ₂ (aq)
5. SbCl ₃ (aq)	 Phenolphthalein in C₂H₅OH
6. AsCl ₃ (aq)	36. KBr (aq)
7. C ₆ H ₆	37. K ₂ Cr ₂ O ₇ (aq)
8. Bromcresol green (aq)	39. KI (aq)
 Ca(OH)₂ (aq) (limewater) 	40. Red dye (aq)
 CCl₄ (avoid contact) 	41. AgNO ₃ (aq)
13. Cl ₂ (aq)	43. NaCl (aq)
15. CuCl ₂ (aq)	44. NaOH (aq)
17. C₂H₅OH	46. Na ₂ S (aq)
22. 6 M HCl	
25. Kerosene oil	47. Starch (aq) (1%)
26. Pb(CH ₃ COO) ₂ (aq)	49. 6 M H ₂ SO ₄

Solids

	SECTION ACCESS
51. Agar (gelatin)	73. CaCO ₃ , limestone
52. Alka-Seltzer	74. Mg ribbon
53. Al wire (thin)	75. MnO ₂
56. NH ₄ NO ₃	81. KMnO ₄
57. BaCl ₂ ·2H ₂ O	82. KCNS
59. Borax, Na ₂ B ₄ O ₇ ·10H ₂ O	84. Silica gel
60. CaO (fresh)	86. NaHCO ₃
62. Carbon (cigarette filter)	87. Na ₂ CO ₃ ·10H ₂ O
63. CoCl ₂ ·6H ₂ O	88. NaOH, pellets
64. Cu wire (thin)	90. NaNO ₂
65. Detergent (soap)	92. Na ₂ SO ₃
66. FeCl₃·6H₂O	93. Na ₂ S ₂ O ₃ 5H ₂ O
67. FeSO ₄ ·7H ₂ O	94. Steelwool
68. Glass wool (or cotton)	95. Sucrose, C ₁₂ H ₂₂ O ₁₁
71. Fe strip	96. Sulfur, flowers
72. Pb foil	99. Zn, granular

¹ ALYEA, H. N., "Tested Overhead Projection Series (TOPS)," (3rd Ed.), Chemical Education Publishing Co., Easton, Pa., 1967. A reprint of all TOPS articles in this Journal from 1962 to June, 1967, available from the Chemical Education Publishing Co., Easton, Pa., \$3.50.

² J. Chem. Educ., 42, A-601-2 (1965). The Macalaster Scientific Corp., 186 Third Ave., Waltham, Mass. 02154, sells a complete set of these 100 chemicals in a case convenient for classroom use; also TOPS devices and projectors.

³ This 1967 UNICELL is simpler than the model published in the J. Chem. Educ., **43**, A 747 (1966).

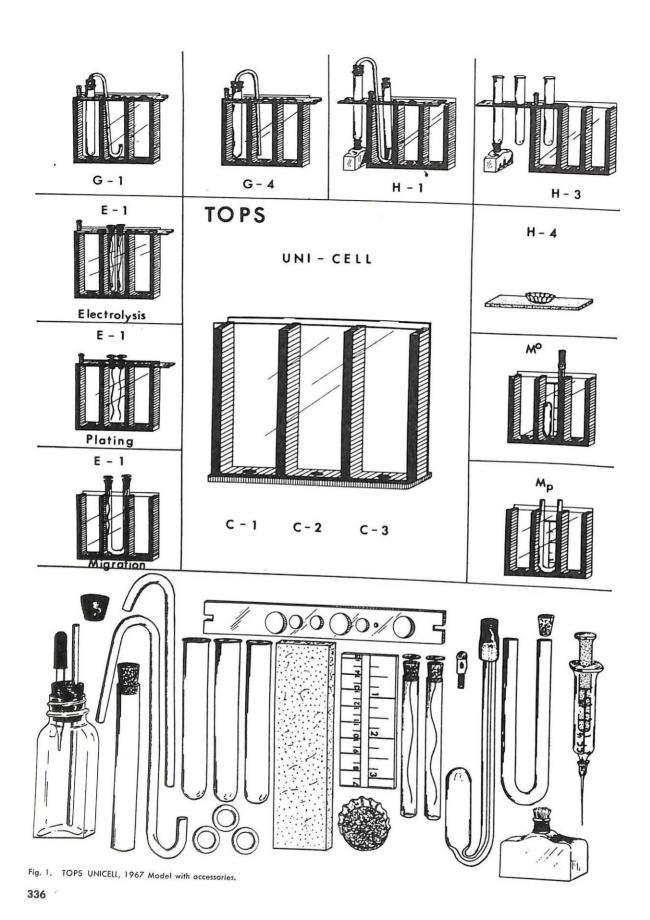
⁴ J. Chem. Educ., 42, A 409 (1965); (b) A 461 (1965); (c) 43, A 349 (1966); (d) Reference in footnote 1.

⁵ References (a)-(c) in footnote 4.

⁶ Daylight projector, quartz-iodine lamp, \$35, J. Chem. Educ., 42, A551 (1965); student dark-room projector, 110-220 v ac floodlight, \$15, ibid., 40, A523 (1963); lensless projector, \$0.50, ibid., 43, A747 (1966).

See footnote 1.
See footnote 6.

⁹ A 12-v quart-iodine automobile headlight can also be used. Spray with heat-resistant paint, leaving a clear window about 4 × 10 mm. Mount with lamp horizontal, projects (as in Fig. 3) on a wall about 1 m sq. A picture-book of 200 TOPS experiments, as shown in this article for nine picture-book experiments will be available by the Fall of 1967. For information write the author of this article, who will reply when the picture-book is available. We are indebted to the National Science Foundation for supporting a project under which most of this TOPS material was developed.



Tested Overhead Projection Series







THE UNICELL

The single device, named the UNICELL, shown in Figure 1, is ample for the teacher when he first adopts the TOPS technique; later he can "graduate" to a more sophisticated 12-device kit described in the TOP series.

Making the Device

The device is made from Plexiglas plastic (polymethylmethacrylate); glass and wood covered with chemically resistant epoxy lacquer can be substituted but is not as satisfactory. If 0.5-cm. or $^{1}/_{e}$ -in. stock is unavailable, cement two 0.25-cm. or $^{1}/_{s}$ -in. sheets together.

- (1) Parts required are four dividers 8 × 1.4 × 0.5 cm, one base 12.5 × 3.3 × 0.5 cm, and two clear sides 12.5 × 8.7 × 0.25 cm. In the top of each divider, bore a hole 1.5 cm deep and thread (the author used a ⁷/₆₄ in. drill and a ⁶/₅₂ tap).
- (2) Cement the four dividers to one plastic side, using the base as a spacer. This is done by holding two pieces firmly together for the count of 100 after running a tiny drop of cement into their juncture from a dropper with a fine point. The cement is made by dissolving 1–5 g of plexiglas in 100 ml of ethane, 1,1,2-trichloroethane, chloroform, or other solvent to give a water-thin solution. The solid end of each divider should be flush with the bottom of the clear piece; the threaded ends will be about 0.7 cm short of the top of the clear side. If any cement smears on the clear side, wipe off at once with tissue paper or cotton.
- (3) After the four dividers are cemented in place, rub them across a piece of fine sandpaper lying flat on the table to make the surface plane.
- (4) Cement the second clear side in place.
- (5) Rub the bottom of the assembled piece on sandpaper to make it flat.
- (6) Cement the base in place.
- (7) Run more cement into all joints, tilting the cell so the cement runs into all cracks to assure tightness.
- (8) Finally, dry for at least an hour before pouring water into the cells to test for leaks.

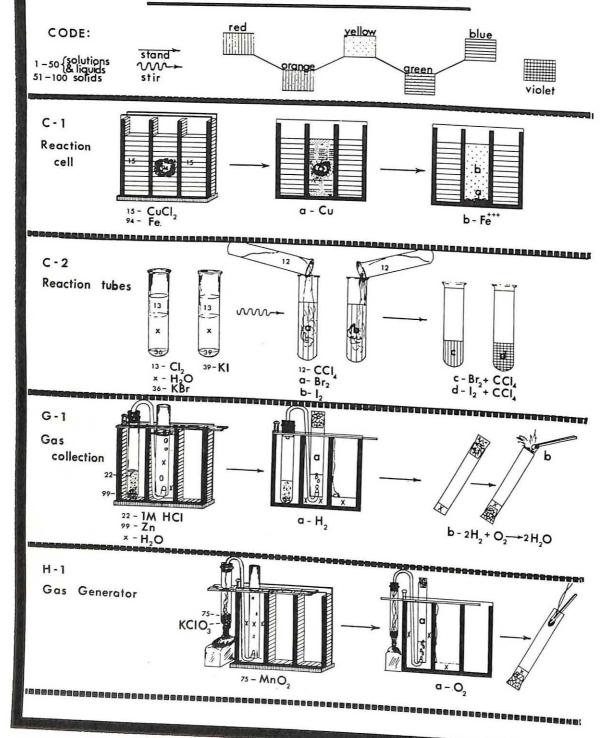
UNICELL Accessories

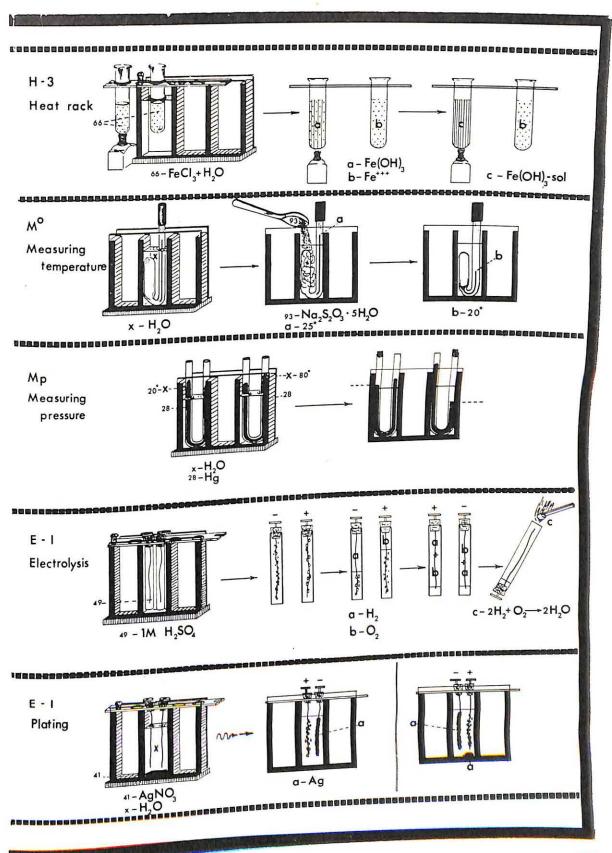
The UNICELL accessories are shown in Figure 1 also. Their dimensions are not critical, and can be judged from the drawings surrounding the UNICELL which show their applications. The designations G-1, H-3, etc., are from the original TOPS articles.⁵ Details of accessories follow.

- (1) A 60-ml wide-mouth bottle with 2-hole stopper, delivery tube with rubber connector and dropper.
- (2) A 1-hole No. 00 rubber stopper.
- (3) A cork-stoppered 12- × 100-mm plastic gas holder.
 (4, 5) 0.5-cm od copper tubing for gas delivery and distillation.
- (6, 7) 12- X 100-mm glass test tubes and rubber O-rings, or sections cut from rubber tubing. Liquids in these tubes will project well only if the tubes are immersed in water in the UNICELL.
- (8) 13- × 3- × 0.4-cm. asbestos stage.
- (9) Transparent scale.
- (10) Coca-Cola cap.
- (11) Two electrodes consisting of 10 cm of 0.02-cm platinum wire passing through a cork to make contact with a thumb tack; 10- × 75-mm plastic or glass tubing.
- (12) Glass thermometer with rubber tubing well. To fill, warm the bulb in the hand, half-fill the well with 50:50 ethyl alchol: red dye (aq). Upon cooling, the liquid descends; remove bubbles by gently blowing the fluid into the bulb, then allowing the fluid to return to the capillary. To remove fluid, warm the bulb, then soak up excess fluid from the well using filter paper.
- (13) U-tube with cork. This is for pressure measurements, as shown in next section.
- (14) Alcohol burner. This can be made from a small glass bottle, notched 1-hole cork, and wick.
- (15) Two to twenty-milliliter hypodermic syringe with No. 24 needle.
- (16) Aluminum plate, 14.8 × 1.8 × 0.1 cm, with three 15-mm holes, 4, 8, and 12 mm from the end; one 3-mm hole 10 cm from the left end; and two slits, 4 × 4 mm, at each end. The latter accommodate:
- (17) A set screw (the author used a ⁶/₃₂ machine screw 2 cm long, with a metal tube 1 cm long crimped on it as shown in Figure 1).

The following simplified substitutes can be made. For item 12: fill a glass vial, 4 cm long X 12 mm od, one-fifth full of red manometer liquid. Insert a glass tubing 15 cm long × 2 mm id passing through a 1-hole No. 00 rubber stopper. This serves as a simple thermometer. Use a similar procedure for item 13, but fill the vial one-quarter full of clean mercury. To measure the vapor pressure of a liquid, e.g., acetone, put a few drops on top of the mercury in the vial (or insert a strip of acetone-moistened filter paper). Immerse the vial in the UNICELL chambers at two different temperatures. For item 16: No. 16 copper wire, or a pipe cleaner wire can be twisted to form a holder for the test tube suspended over the burner; screw 17 passes through a smaller loop. For suspending the two electrolysis tubes a pipe cleaner can be twisted into a double loop, with ends resting on the two middle dividers.

PICTURE-BOOK EXPERIMENTS







STUDENT WORKBOOK

Questions

Demonstrations, properly conducted, involve active student participation just as much as any class "experiment" or "experience." The TOPS UNICELL makes it possible for each student, individually, to carry out the experiment on the writing arm of his lecture-room desk. The teacher projects it to confirm student observations.

The reaction between Fe and Cu²⁺ is given here as an example. In the old, conventional, macro-demonstration the lecturer lifted an iron bar from blue cupric solution to demonstrate that the iron had been coated with red Cu. Contrast this with the corresponding UNI-CELL demonstration; note the research experience in which the student is involved below.

The experiment is the first one in the Picture-Book Experiments shown on the two preceding pages. The student must answer questions relating to the following diagram, Figure 2.

Observations

- 1-14. Colors?
 - 15. Temperature in cells?
 - 16. Physical changes?

Explanations

- 17. Colors?
- 18. Chemical equation, including flow of electrons?
- 19. Why is 6, 7 green?
- 20. Why do the steelwool fibers suddenly and explosively crumble?
- 21. Why does some of the yellow solution stream up-

wards (toward 5) whereas other of the yellow solution streams downwards (toward 12)?

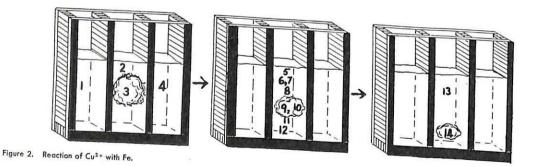
Research

22. Suggest researches, preferably with results amenable to graphing, suggested by your observations. You will be sent to the laboratory, in groups of five, to carry these researches out.

Homework

Consult tables of electromotive force, atomic weights (round off to three digits), and heats of reaction.

- List ten cations, with their half-cell potentials in descending order of chemical activity.
- 24. What voltages would cells, made of the following pairs of metals, give: Cu-Zn, Mg-Ag, Al-Cu?
- Name three metals which would behave like steelwool in displacing Cu²⁺. Three of which would not.
- 26. Assume that the middle chamber of the UNI-CELL contained 10 ml of solution with 1.7 g of CuCl₂·2H₂O, that 1 g of steelwool was used, and that the temperature rose 12°C. How many moles of Cu²⁺ and of Fe were present at the start of the reaction? At the end, assuming Cu + Fe²⁺ formed (the Fe²⁺ later oxidized to Fe³⁺ in solution)? What weights of Cu or Fe remained?
- 27. What was the heat of reaction per mole of Cu²⁺?
 Contrast this with the accepted published values.
 Account for any difference in the two values.



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TEACHER'S MANUAL

Answers

General Instructions to the Teacher

Notice that there are three phases:

- 1. The Experiment. Carried out by each student in his own UNICELL. Then, in teams of five, using a lensless projector (see next page). Finally, by the teacher who projects his UNICELL to a 2×2 m size on the side wall while the student records observations and explanations.
- 2. Research. Suggested, planned, and earried out by the students in teams of five each, working an hour in the laboratory. Teams return to report their findings to the class.
- 3. Homework. A report of his research, and answers to homework questions involving reference work and mathematical calculations.

Special Instructions for the Fe + Cu2+ Experiment

- Use CuCl₂ (aq) diluted to blue, not green. Use coarse (Grade No. 1) steelwool, loosely rolled.
- 2. After reaction has occurred, exhibit the UNI-CELL: the red Cu is visible. Have a student feel it (center chamber is warmer). Use the thermometer to find the temperatures of the cell chambers; have the class record the results.
- 3. Rinse the cell out at once or the plastic will soil.

Student Workbook: Answers to Questions

The student may give the following answers.

- 1. Blue, Cu2+.
- 2. Blue, Cu2+
- 3. Grev. Fe solid.
- 4. Blue, Cu2+.
- 5. Yellow, Fe³⁺
- 6. Green, blue Cu^{2+} + yellow Fe^{3+} .
- 7. Ditto.
- 8. Yellow, Fe³⁺.
- 9. Red, Cu solid.
- 10. Grey, Fe solid.
- 11. Blue, Cu²⁺.
- 12. Yellow, Fe³⁺.
- 13. Yellow, Fe³⁺.
- 14. Red, Cu solid.
- Middle cell temperature rose 12°C.
- 16. Fibers tore loose, almost explosively, from the ball of steelwool. Yellow solutions streamed upwards and downwards from the ball of steelwool. A layer of yellow solution formed on top. The ball of metal finally collapsed and sunk to the bottom of the chamber, as red mud (Cu-coated Fe).

Explanations

- 17. See 1-14 above.
- 18. Fe + Cu²⁺ \rightarrow Cu + Fe²⁺ which oxidized to Fe³⁺.
- 19. Blue Cu²⁺ + yellow Fe³⁺ gave a green solution.
- 20. Heat of reaction and resulting convection currents ejected the crumbling fibers.
- 21. Fe³⁺ solution, hot from heat of reaction, was less dense than the original Cu2+ solution and streamed upwards. On the underside of the steelwool the iron absorbed the heat, and the colder, more dense, Fe3+ solution streamed downwards.

Research

- 22. Researches suggested by, and subsequently carried out by, the students might be the following.
 - (a) Place yellow Fe3+ in the outer compartments. Graph reaction of steelwool with varying Cu2+ concentrations versus time for the middle compartment to reach this yellow color.
 - (b) Same as above, with varying grades of fineness of steelwool.
 - (c) Same as above with H+ or other ions added to the solution.
 - (d) Same as above with the initial temperatures of the Cu2+ at 0, 25, and 60°C.
 - (e) Contrast Al, Mg, and Fe reacting with Cu^{2+} .
 - (f) Measure, using the UNICELL M° accessory. the heat of reaction under varying factors mentioned above.

Homework Answers

- 23. K, 2.92; Na, 2.71; Mg, 2.34; Al, 1.67; Zn, 0.76; H, 0; Cu, -0.34; Ag, -0.80; Pt, -1.2; Au,
- 24. Cu-Zn gives 1.1 volts; Mg-Ag, 3.41 volts; Al-Cu, 2.01 volts.
- 25. Mg, Zn, and Al would displace Cu2+; Ag, Au, and Pt would not.
- 26. Moles of $Cu^{2+} = 1.7/170 = 0.01$. Moles of Fe = 1.0 55.9 = 0.018. The Fe was in excess. Moles of Fe remaining = $0.018 \times 55/8 = 0.045$
- 27. Heat of reaction per mole of Cu^{2+} is 10 ml \times 12°C 0.01 = 12.000 calories. Literature value is 18,000 calories. These two values differ because much heat was lost by radiation, the weight of Fe or concentration of Cu2+ solution differs from that of water, the Fe was heated up but was not accounted for in the calculation, etc.

PROJECTORS

Commercial Models: The more expensive overhead projectors suitable for chemical experiments cost \$150-400 and usually have a brilliant "daylight" quartziodine 110-v ac lamp costing about \$8 and lasting about 80 hr. The less expensive models cost about \$100, use a one dollar, 150-w, 110-200 v ac floodlight with 2000-hr lifetime; they must be operated in a nearly darkened room and are recommended only for students or for teachers with a limited budget. Suppliers include the Laboratory Furniture Co., Old Country Road, Mineola, N. Y.; the Macalaster Scientific Corp., 186 Third Ave.; Waltham, Mass., the Central Scientific Co. (CENCO) 1700 Irving Park Road, Chicago, Ill.; the Thermofax division of the Minnesota Mining and Manufacturing Co. (3 M), St. Paul, Minn., and branch offices: the Edmund Scientific Co., Barrington, N. J. 08007; the Charles Beseler Co., East Orange, N. J.; Hugh Wood, Ltd. (Ealing) 23 Lehman Street, London E-1, England; the Technifax Corp., Holyoke, Mass.; and others.

Homemade Projectors. 6 Both the daylight quartziodine projector and the 150-w spotlight projector shown in Figure 3 can be built in a few hours for about \$35 and \$15, respectively. Lenses, lamp, and reflector are available from the Edmund Scientific Co., Barrington, N. J. 08007, and the ventilating fan, a Skipper Venturi SKR can be purchased from Radio-Electric, 7th and Arch Streets, Philadelphia, Pa. Full details are given in the TOPS reprint7 and TOPS articles.8

A Lensless Projector. A satisfactory, inexpensive (half a dollar!) projector is shown in Figure 3. It is simply a single-filament automobile bulb (No. TS 1133 or TS 1183) to which two wires are soldered, leading to a 6-v source (a 6-v de automobile battery, or battery charger output, or 6-v ac from a transformer plugged into 110 or 220 v ac). The bulb is sprayed with heatresistant lacquer leaving a clear area 10 mm in diameter in the center of the bulb. A rubber tubing is slipped over the base, which fits into a slot as shown in Figure 3. The plywood base is $40 \times 15 \times 0.5$ cm; the stage is 15 \times 4 \times 2 cm and is 14 cm from the screen. The slotted bulb-support is $15 \times 2 \times 2.5$ cm. A translucent paper screen is placed 40 cm from the bulb, and the reaction vessel interposed. Reactions can be seen in color on the screen even in a large auditorium, and depth of focus is several times that of conventional projectors.9

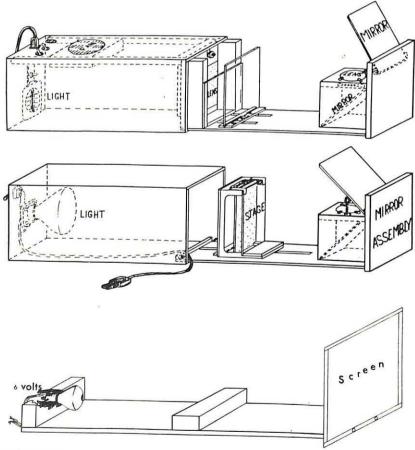


Figure 3. Three homemade projectors.

Figure 3. Three homemade projectors.

Top: A quartz-iodine lamp is employed in this daylight projector; cost to make, \$35.00. Its construction was described in this Journal, 41, A551 Center:

student projector for a dark room is made with a 150-w spotlight as a light source, cost \$15.00. Its construction was described in this Journal, 40, A523 (1963). Bottom:

A lensless projector using a 6-v automobile lamp as a source, cost, \$0.50.

The Emperor's New Clothes— A critical review of programmed books

G M Seddon

A cursory examination of many existing programmes shows that there is among programme writers a fairly wide-spread misunderstanding and misapplication of the principles upon which programmed instruction is based. Furthermore, these principles do not automatically lead to the most efficient learning, for in some cases doing the exact opposite has a better effect. Thus with programmed instruction as presently practised, we are experiencing an educational example of the old story about the Emperor's new clothes and at the moment, despite all the bally-hoo, there is really only one valid criterion by which a programme can be assessed or indeed differentiated from a normal textbook. This is the fact that it has been tested and shown to work.

CONVENTIONAL BOOKS are intended to fulfil several objectives and are clearly meant for the edification of both teachers and students. For example, they act as a source of reference material and problems as well as being a teaching medium. Programmed books, on the other hand, are intended solely for the student and to help him learn something specific, i.e. to change his behaviour in a carefully specified way. Whereas the author of a conventional textbook might think in terms of telling the student all that he is expected to know, the good programme writer begins by defining the specific task or tasks which the student will be able to do on completing the programme. A chapter in a conventional textbook might be intended rather vaguely to give the student an understanding of the basic principles of structural isomerism. On the other hand, the programme writer first thinks about what this means in more detail and asks himself the question, 'What does the student have to do in order to demonstrate his understanding of the basic principles of structural isomerism?' The answer to this question constitutes the programme writer's objective for the complete programme, or for each step through which the student passes.

In order to test for real understanding—at any level of abstraction—the student must carry out a series of acts of discrimination, i.e. he should be able to identify positive and negative instances of a rule, principle or concept. Thus in the instance given previously the objective should be written as in the instance of the previously the objective should be written.

be written as in Fig. 1.

A principal fault with many existing programmes is that their objectives have never been formulated in these

Mr Seddon is research fellow at the National Centre for Programmed Learning, School of Education, University of Birmingham. Fig. 1

AN OBJECTIVE

Given a selection of structural formulae the student must be able to identify those molecules which are structural isomers.

Fig. 2

2-1

Molecules having the same molecular formula but different arrangements of the atoms within the molecule are said to be STRUCTURAL ISOMERS. For example $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3 are structural isomers because they both have the molecular formula $\text{C}_2\text{H}_6\text{O}$.

Similarly $\mathrm{CH_3CH_2CHO}$ and $\mathrm{CH_3CH_3}$ are

structural isomers because they both have the molecular formulae—

2-2

CH₃ CH₂ CHO and CH₃ C CH₃

both have the

2-3

Molecules having the same molecular formula but different arrangements of the atoms within the molecule are said to be STRUCTURAL ISOMERS.

Which of the following molecules are structural isomers?

(i) $\operatorname{CH_3} \operatorname{C} \operatorname{CH_3}$ (ii) $\operatorname{CH_3} \operatorname{CH_2} \operatorname{C} \operatorname{CH_3}$ O O (iv) $\operatorname{CH_3} \operatorname{CH_2} \operatorname{OH}$

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Fig. 3

3-1

Aldehydes that have no a-hydrogen atoms (A) disproportionate in the presence of strong (B) base (C) to give equal amounts (D) of the corresponding alcohol (E) and carboxylic acid (F).

Complete the following equation:

2(CH₃)₃CCHO+NaOH-----

3-2

Aldehydes

in the presence of

give equal amounts of corresponding alcohol and carboxylic acid.

Complete the following equation:

2(CH₃)₃CCHO+NaOH---->

3-3

Aldehydes that have no \alpha-hydrogen atoms (A) disproportionate in the presence of strong (B) base (C) to give equal (D) amounts of the corresponding alcohol (E) and carboxylic acid (F). Complete each of the following equations if you

(i) 2CH₃CHO +NaOH -→(testing A, D, E, F)

+KOH —→(testing all points)

(iii) 2(CH₃)₃CHO+NH₄OH-→(testing B, D, E, F)

(iv) $2CI_3CCHO +H_3O^+ \longrightarrow (testing C, D, E, F)$

Fig. 4

4-1

Molecules having the same molecular formula but different arrangements of the atoms within the molecule are said to be the STRUCTURAL ISOMERS of one another.

For example $\mathrm{CH_3CH_2OH}$ and $\mathrm{CH_3OCH_3}$ are STRUCTURAL ISOMERS because they both have the molecular formula, C3H6O.

4-2

STRUCTURAL

ISOMERS

precise behavourial terms, or if they have, no emphasis has been placed upon discrimination. Instead, the objective has emphasized verbalization of the rules or principles or the rehearsal of technical terms. Clearly these parrot-like activities do not necessarily require any understanding of what the rules, principles or names represent. Consequently, if the author of such a programme has never been clear about what real understanding means in behavourial terms, it is hardly surprising if students who work through the programme fail to show any real understanding afterwards.

Student responses

In all types of programme the student proceeds through a sequence of problems or frames to test his understanding at each stage, and by inspecting the answers given by the students to each frame the programme writer is helped in revising the initial draft. In common-sense terms the response required of the student ought to demonstrate unequivocally whether or not he can do the particular task which was specified as a sub-objective for that stage of the programme. It is surprising how in a large number of existing programmes the authors have lost sight of this simple fact and have constructed many frames which are quite useless for this purpose.

Examples of this common mistake are given in frames 2-1 and 3-1 (Figs 2 and 3). Frames 2-2 and 3-2 show just how much of the information presented in each case is necessary in order for the student to respond correctly. In both the original frames important material, which the student is obviously supposed to learn and understand, can be omitted or blacked out without affecting the probability of the student responding correctly. If in writing frame 2-1 the author had defined his objective more carefully and as an act of discrimination, the mistake would not have happened. Using the objective of Figure 1 we can automatically write an introductory frame such as frame 2-3. Here we have a frame which is useful to the programmer on revising the first draft, and one which is straightforward and yet demanding for a student.

In frame 3-1 several new steps (each lettered A, B, C, etc.) are presented at once. While this is not necessarily a bad thing from the student's point of view, the frame is bad from the programmer's point of view, because the required response tells us absolutely nothing about the student's understanding of points A, B and C. To do this the frame would have to be re-written as in frame 3-3. This clearly tests every new point.

A third illustration of bad technique is illustrated in Fig. 4. Frame 4-1 illustrates the use of initial letters of technical terms in order to help or 'prompt' the student. However, experiments by Kemp and Holland¹ have shown that students who are used to such programmes can respond correctly to frames like 4-2 in which the important material of frame 4-1 has been blacked out. In frame 4-1, therefore, the student may be responding correctly but for the wrong reason. Obviously frame 4-1 is quite useless in telling the programmer about whether or not the student underCHEMISTRY IN BRITAIN

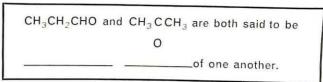
stands. This black-out ratio has been proposed as being a measure of the extent to which a book is programmed so that unprogrammed material can be differentiated from programmed material.

Finally, existing programmes seem to have built up an image of themselves as being strings of sentences with blanks in them as in Fig. 5. On reflection this kind of technique is clearly bad, because such frames test the student's ability to solve crossword puzzles on top of the more relevant task of demonstrating mastery of the objective. It is conceivable—and in practice this actually happens-that students who are quite capable of answering direct questions may be incapable of playing the guessing game required in Fig. 5. For this reason such frames should not be written because they may fail to provide the programmer with the information he needs about the student's progress at any stage. Such frames are contrived and stereotyped as well as being totally irrelevant to what we really want the students to be able to do. With this kind of frame there is a strong tendency towards rote learning-an undesirable element which can be removed only by asking the student a direct question and forcing him to carry out an act of discrimination. This view of frame writing may resolve the early controversy about whether students should construct their responses or whether they should be allowed to select their answers from a range of given alternatives. The argument against multiple-choice questions was that they required a lower level of intellectual activity than did constructed response items. However, as we have seen, on looking closely at most objectives requiring understanding, they generally involve an act of discrimination. This obviously requires a multiple-choice question.

So far, frames have been discussed in common-sense terms from the point of view of the amount of information which the programme writer or teacher can obtain from the student's response. However, we would come to the same decisions about the frames using principles from learning theory, in the sense that learning is supposed to take place more efficiently when the student makes an active response as opposed to just reading. In the bad frames discussed previously the student is not forced to respond actively in the relevant way. Hence less efficient learning would be predicted from these frames than from the frames which it is suggested are better.

To some extent, research findings support this view. For example Holland² prepared three versions of the same programme so that one version (A) required critical relevant responses for every frame as in frame 2–3. In another version (B), the student was required to make irrelevant or trivial responses as in frame 2–1, and in the third version (C) no active responses were required at all; here the students merely read complete statements. On comparing the results on a final post test the students who worked through version A were significantly better than the others. Furthermore, the difference was significant at the 0-001 level; *i.e.* the chances were less than one in a thousand that these differences arose because of errors made in trying to assign students at random to each group. The

Fig. 5



results of Krumboltz3 were in agreement on making trivial responses but not with regard to the students who merely read. With these latter there was no difference from those who had responded actively and relevantly. There are several other studies which have shown that reading is iust as effective as making active relevant responses. However, they have often employed short programmes which did not allow the students to become inattentive. or they involved mature students who had considerable background knowledge of the subject matter. This kind of student naturally thinks about what he is reading in that he continually seeks relationships between the new material and his previous knowledge or tries to reconcile apparent contradictions with what he has read elsewhere. Surely, this is active responding. This view is currently being supported by the research findings of Leith4 and his co-workers at the National Centre for Programmed Learning.

To sum up, the demand that the student should make an active relevant response is probably most necessary for students who are beginning a fairly new field where no closely relevant background concepts are well established. Otherwise reading may be adequate or even superior, because the tedium of continually making active responses may actually interfere with the learning.

Logical sequence

Another basic principle of programmed instruction is that the material should be presented in a carefully prepared logical sequence and several algorithmic techniques for constructing 'logical' sequences have been devised. Such ingenuity may be rendered futile by the results of some studies5,6,7-admittedly using only short programmes-which have shown no significant superiority for logically-ordered presentations over versions of the same programme in which the frames have been scrambled into a completely random sequence. In one case8 in which the extent of this re-arrangement was relatively small the final performance of students who worked through it was significantly better. A study by Mager9 must remove any complacency about the ability of a programmer to devise a sequence which his students will find logical. Mager found that successful sequences devised by students themselves were quite different to those sequences which he had previously prepared for them.

Another equally basic assumption is that students learn most efficiently when they are given the answers to frames as soon as they have made an attempt at each one. However, Jacobs and Kulkarni⁸ found that students who were

not given answers in one particular programme had learnt significantly more than students who had been given continual immediate confirmation. Moreover, on an attitude test the students, who were not given answers were more favourably inclined towards programmed instruction than those who had been given answers.

Finally there is the postulate that students learn best by making a minimum number of errors as they work through the programme, and that a good programme is one in which less than 5 per cent of the students respond incorrectly for any one frame. Elley10 has shown that while this principle is probably true for the rote learning of nonsense syllables, it is not so necessary for the learning of meaningful material presented in programmes. McGuigan and Peters¹¹ have shown that the correlation between the error rate on the programme and the final gain in knowledge as measured by pre- and post-tests is -0.23. Thus, as a broad generalization, fewer errors made on the programme lead to a higher performance on a final post-test. However for a correlation as low as this only the most vague predictions of the final post-test performance can be made knowing the error rate on the frames.

To be fair, not all the research on issues such as these has shown such conflict between theory and experimental observations. On the whole there is a reasonable amount of agreement. These examples of disagreement have been presented to illustrate that these principles themselves do not constitute a general panacea.

Perhaps the research on these issue of logical sequencing, immediate confirmation and low enres can be reconciled when it is realized that the char es which produced more efficient learning required the saidents to think more actively about what they were reading. They also illustrate very well that for both expert and layman alike it is very difficult to make reliable predictions of the likely effect of any piece of teaching material just by making a casual observation. There are three spectacular instances in which subjective judgements of experts have been shown to be quite wrong. In the U.S.A., Maier and Jacobs12 asked some members of a 'well known and highly respected centre for the study of programmed instruction' to revise a programme according to any criteria which they thought would bring about an improvement. On testing the revised programme it was found that the error rate had increased from 5.7 to 7.1 per cent. There was no improvement in the final performance on a post-test or in the attitudes of students towards programmed instruction. In another case Rothkopf13 presented seven different versions of the same programme to 12 high school teachers who had just completed a three-week course on programmed instruction. Each teacher was asked to read through the different versions and to rank them in order of merit. On comparing these subjective assessments with those which had been obtained from previous testing, the rank correlation coefficient between the two sets of judgements was -0.75, i.e. the subjective assessments were practically the reverse of the objective assessments. Perhaps the most startling instance is reported by Roebuck¹⁴ who showed that using a programme prepared by professional programme writers, students, who had a mean score of 14.0 per cent on a pre-test, scored only 12.0 per cent on the same test after working through the programme.

Conclusion

The obvious conclusion to be drawn from all this research is that programmed instruction is in a very confused state about what constitutes good and bad teaching technique. These are issues for research which it is hoped will be cleared up fairly soon, and it may well mean that, as a result, future programmes will look very unlike the specimens at present available. For example, we should certainly hope that all the elementary mistakes in so many of the frames will disappear. However, there is no doubt that in one very important aspect existing programmes, no matter how imperfect, are very different from conventional books because they have been tested, they have been shown to work, and objective data on their observed effectiveness is available. Indeed, at present this is the only justification for buying a programme rather than a normal book, for, as we have seen, a conventional presentation of the subject matter sometimes teaches just

Publishers have been recommended many times to supply these pre- and post-test results to the purchasers of programmes and some are already doing so. Shortly the National Centre for Programmed Learning will begin an evaluation scheme and will set up an information centre to receive the objective data obtained by users of existing programmes and send it out to potential purchasers. Similarly the Royal Institute of Chemistry has a scheme in which unpublished programmes are circulated among schools, colleges and universities for testing. Each of these schemes has one aim in view—to improve the present practice and standards. Obviously only evaluation and testing can bring this about.

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EXPERIENCES IN PROGRAMMED CHEMISTRY TEACHING

by V.I. Levashev

Our methodology for programmed chemistry teaching is based on the following considerations:

1. The lesson is the basic method of teaching and education. The teacher offers programmed instruction for exercises and practical work.

The effectiveness of the method can be assessed from the results obtained

by the students being trained.

3. Programmed instruction is one method of teaching, and it is used only in those cases where it is more effective than other methods.

The object of our experiment was to discover in what form and to what extent the programmed method could be used in chemistry teaching. We decided to use a teaching machine and wrote programmes for difficult chapters in the Class VIII (15-16 years age group) chemistry course for which there is a programmed textbook.

Programmed Teaching of New Material Programmed teaching helps the teacher to introduce new material and to test whether it has been assimilated. Topics have to be arranged in a strictly logical order, and this preparation helps the teacher to install a 'feed-back' into the system - (teacher-pupils-teacher) so that he can check how his pupils are progressing. We try to choose short and simple experiments and we exclude exercises with lengthy calculations

Our work can be judged by considering the plan of one of twenty programmes on the theme 'chemistry and agriculture' which we gave to Class VIII during 1964/65. This lesson required the use of 36 machines and a set of cards with test questions for each section of the lesson.

TOPIC: The Identification of Mineral Fertilizers Samples of mineral fertilizers, solutions of sulphuric and nitric acids, caustic soda, sodium chloride, barium chloride and silver nitrate, copper turnings and wire should be available.

Plan of the Lesson

- 1. Find out what pupils know about nitrogen, phosphate and potassium fertilizers.
- 2. Give examples to show why it is important to be able to identify mineral fertilizers.
- 3. Reactions used to identify ammonium nitrate and ammonium sulphate. Demonstrations of the reactions of these salts. The teacher then asks the pupils to check these observations against information given on a card. He then asks questions 1, 2 and 3 (see later).
- 4. Identification of nitrogen fertilizers. Demonstration of the analysis of sodium nitrate and ammonium sulphate. Check with the card; question 4.
- 5. Reactions of phosphates; identification of phosphate fertilizers. Demonstration of the reaction of silver nitrate solution with phosphates. Determination of superphosphate. Comparison with card and questions.
- 6. Reactions of chlorides. Identification of potassium fertilizers. Flame test for sodium and potassium salts.
- 7. Draw general conclusions concerning the methods of analysing mineral fertilizers.
- 8. Test the pupils' knowledge of the material with a special test card of 10 questions.
- 9. Explain the practical work to be done on this topic.

Homework: The following are typical questions on the card supplied:-

1. A smell of ammonia is obtained when a fertilizer is heated with alkali. Why? The fertilizer is:- (a) a sulphate, (b) a nitrate, (c) an ammonium salt, (d) a chloride.

- 2. A brown gas is evolved when a fertilizer is heated with copper and sulphuric acid. Why? The fertilizer is:- (a) a sulphate, (b) a nitrate, (c) an ammonium salt, (d) a chloride.
- 3. Addition of barium chloride to a solution of an unknown fertilizer gives a white curdy precipitate. Why? The fertilizer is:- (a) a sulphate, (b) a nitrate, (c) an ammonium salt, (d) a chloride.
- 4. A smell of ammonia is obtained by heating a fertilizer with alkali, and brown fumes when it is heated with copper and sulphuric acid. Which fertilizer have you got? (a) ammonium sulphate, (b) sodium nitrate, (c) urea, (d) ammonium nitrate.

Each section of the topic ends with a test. The pupil marks his card with what he thinks are the correct answers and then switches on the machine to check if he is correct. The teacher moves on to a new section when he is sure that previous sections have been understood and that all mistakes have been corrected. Ten questions are answered at the end of the lesson by way of recapitulation.

The effectiveness of these lessons can be judged from the fact that in 1964/65 we spent only 10 periods on the difficult topic 'classification of substances' in class VII instead of the 16 periods allocated in the syllabus. We used to allow 4-5 periods for the revision of this topic but in the 1965/66 school year we only needed 2 revision periods. This year we are spending only 15 periods on the difficult topic 'properties of acids, bases and salts' in contrast to 22 which were previously required. We included 'ammonia and ammonium salts' in this topic to give students better preparation for the 'chemistry in agriculture' course. Our students got high marks in the course on mineral fertilizers even though no textbook material was available.

Two years' experience of teaching difficult topics in classes VII and VIII chemistry courses by the programmed method shows that it gives good results and may succeed in raising the level of the students' knowledge of these topics.

The 'feed-back' system we use - teacher-pupil-teacher - has its opponents. They object to the inclusion of test questions on the grounds that the pupils may also remember incorrect answers. This is not a very convincing argument because the process of cognition involves a comparison of known and unknown, correct and incorrect, and one of the tasks of school education is to teach pupils how to select a correct answer from a number of

incorrect ones in everyday life. We claim that our experience in dozens of lessons shows that these objections to the inclusion of test questions are groundless. The method has its shortcomings however: e.g., the answers do not necessarily represent the state of the pupils' knowledge as it might be exhibited in an oral or a written examination. At the same time it does give an opportunity to check up on the progress of all members of the class in a short time.

We defend the 'feed-back' method using multiple choice questions but we do not exclude the possibility of using other methods of checking answers and solutions to problems. All these methods have their advantages and disadvantages which the teacher can evaluate in the course of his work.

Combining Programmed Lessons with Ordinary Lessons In our experience the best results are obtained by combining programmed lessons with ordinary lessons. Examples of such combinations are the courses we give on 'chemistry and agriculture' and 'properties of acids, bases, salts and oxides', in class VIII. The first topic was easily programmed. We divided it into 13 lessons of which 3 were ordinary. The 6th lesson consisted of practical work on 'the identification of fertilizers'; lesson 12 was a test and lesson 13 a discussion of the test results and a final summary. In the second topic only 6 out of 13 lessons were programmed. These were concerned with the properties of acids, bases, anhydrides, basic oxides, ammonia and ammonium salts. The programmed lessons included experimental problems and a written test with a discussion of the results. A final talk on the topic was organised as an ordinary lesson.

We have obtained good results by combining the two types of lesson with a 30% saving in time. In future other topics may be treated by this method, but only if the results show that good results can be obtained. One of the important problems for teachers who use these methods is to identify methods of teaching them.

Individual Programmes Experiments on programming work for individual pupils in order to fill gaps in their knowledge have given good results. For example, these gaps usually occur in the class IX topic 'Oxides, acids, bases and salts'. A competent teacher starts by revising this topic in class IX, but even then there may still be some students who have not assimilated all the material. The teacher has to organize additional lessons, but these do not always solve the problem. During the 1964/65 school year

we decided to organise programmed courses and tests for individual pupils.

He is given a typed question paper and works with it for half-an-hour, checking his answers with the machine. He then shows his notebook to the teacher. If there are no bad mistakes he moves on to another section, but if there are a lot of errors he is told to work for a longer period on the paper. Eight lessons of this type were organized for 16 pupils with gaps in their knowledge; of these 12 got good marks and 4 satisfactory marks. They were working on their own, whereas a large number of additional lessons of the ordinary type would have been needed to achieve the same results. Preparation of the material involves the teacher in a lot of work, but once it is done it can be used again in subsequent years. New groups of pupils have used these programmes in 1965/66 with good results.

Individual work on the topic 'Foundations of the theory of electrolytic dissociation' in class IX was organized without programmed instruction, but with the help of annotated questions in a textbook and a teaching machine for display of the correct answers. This method has been quite successful.

Programmed Aids in School We decided to create logical programmed school aids on difficult topics in the chemistry course and we have now written programmes for 'classification of chemical substances' for class VII, 'properties of acids, bases, salts and oxides' and 'chemistry in agriculture' for class VIII. We would like to say something about the preparation and use of these aids. First of all it is necessary to pay special attention to the 'feed-back' system - pupil-textbook-pupil. We do not include any discussion of incorrect answers in the text material and we try to keep this text material as concise as possible. We find that effective feed-back can be got from concise texts and a teaching machine.

The material in our aids is quite similar to conventional texts but it is compiled in a more logical way and is shorter. The material for a given lesson is divided into sections which conclude with test questions. Multiple answers (2-4), only one being correct, are provided.

We divide the topic 'oxides' into the following sections:- what are oxides?, formation of oxides in combustion and decomposition reactions, oxides of Metals and non-metals, formulae and names, oxides in nature and in life. Questions and answers of the following type are included in the first section:-

1. Which of the given substances is an oxide and why?

(a)
$$\text{Al}_2\text{O}_3$$
, (b) AlCl_3 , (c) $\text{Al}(\text{OH})_3$, (d) CaO_3 , (e) P_2O_5 ,

(f)
$$SO_3$$
 , (g) H_2SO_4 .

Experience shows that a test which covers all sections of the course can easily be organized with the aid of a teaching machine.

Since the machine evaluates answers only in terms of the words 'correct' or 'incorrect' we include in the text material questions not intended for the machine. These questions are supplemented by notes which indicate where the relevant material associated with this question may be found in the text. We conclude that textbooks similar to our programmed school aids are more effective than the conventional ones even if teaching machines are not used. Not all topics are suitable for the programmed method, and we think that textbooks should include both programmed and unprogrammed material.

SCIENCE TEACHERS' ABSTRACTS

RÉSUMÉS POUR PROFESSEURS DE SCIENCES

These abstracts are prepared by teachers for teachers and are published and circulated (in Great Britain only) by the Education Services division of the Esso Petroleum Company Ltd. A typical issue has sections on biology, chemistry, mathematics and physics. The April 1968 issue contains 79 biology abstracts, 229 chemistry, 161 physics and 52 mathematics, together with notices of new books.

Two pages are reproduced here, not so much for the sake of the abstracts themselves, which refer to papers published in 1967, but as an example of what can be done through the co-operation of enthusiastic teachers and enlightened industrial organizations. We are grateful to Dr. D. R. Browning, the General Editor, Dr. D. Miller the Chemistry Section editor and to the Esso Petroleum Company for permission to reproduce this extract. Dr. Browning has contributed the following

"The Esso Science Teachers Abstract Service was instituted because it was felt that although teachers must keep up to date, it was impossible for them to find time to search through even the normal abstract literature or to assess the value of the material taken from such abstracts in a teaching situation. For this reason an abstract service where articles are abstracted because of their value to the teacher was considered essential. The scope of this journal is to be widened in Science and Technology. Here again the criterion for inclusion in the journal will be the value of the paper for teachers."

Ces résumés analytiques, faits par des enseignants à l'intention d'autres enseignants, sont publiés et diffusés (en Grande-Bretagne uniquement) par la Division des services pédagogiques de la Esso Petroleum Company Ltd. Chaque numéro comprend habituellement des sections consacrées à la biologie, à la chimie, aux mathématiques et à la physique. Le numéro d'avril 1968 contient 79 analyses touchant à la biologie, 229 à la chimie, 161 à la physique et 52 aux mathématiques, ainsi que des notices sur de nouveaux ouvrages.

Nous reproduisons deux pages de ce numéro, moins pour leur contenu même (les analyses se rapportent en effet à des études parues en 1967) que comme exemple des résultats que peut fournir la coopération d'enseignants enthousiastes et d'organisations industrielles éclairées. Nous remercions M. D. R. Browning, rédacteur en chef, M. D. Miller, rédacteur de la section consacrée à la chimie, et la Esso Petroleum Company d'avoir autorisé la reproduction de cet extrait. M. Browning nous a fait parvenir l'avant-propos suivant: « La compagnie Esso a créé un service d'analyses destinées

aux professeurs de sciences parce qu'il est apparu que ces enseignants, qui doivent pourtant tenir leurs connaissances à jour, ne disposent même pas du temps nécessaire pour faire des recherches dans les collections habituelles d'analyses, ni pour évaluer la valeur pédagogique de l'information ainsi recueillie. Aussi a-t-il semblé indispensable de créer un service qui choisisse les articles à analyser en fonction de leur valeur pédagogique. Le champ couvert par la revue s'élargira dans un proche avenir pour faire de celle-ci un répertoire des sources d'information scientifique et technologique. Le critère adopté pour la sélection des articles sera toujours l'intérêt que ces articles présentent pour l'enseignant. »

- C100 System Triethylamine Water: Equilibrium Diagram and
- Some Physical Properties

 Gives details of the freezing point diagram and corroborates the existence of the dihydrate. Critical solution temperature 18.3°C.

 Kartzmark, E.M. Canad. J. Chem., 45 1089-1091 (1967)
- Shows that the catalyst may be promoted by the addition of magnesia. Triple promotion using magnesium oxide, potassium oxide and silica works if the proportions are right. The best catalyst was a reduced mixture of iron with 2% MgO, 1% SiO₂, 1% K₂O by weight and containing FeII/FeIII in the ratio 0.535:1.

 Bull. Chem. Soc., Japan, 37 653 (1964)
- Clo2 Determination of the Solubility of Sodium Hypophosphates

 and the Study of Their Hydrates

 The solubilities of the tetrasodium, trisodium and disodium salts have been determined. All show a discontinuity indicating a change of structure.

 Holloway, J. and Lee, J.D.

 J. Chem. Soc., (A) 6 923-925 (1967)
- C103 Multiple-Choice Tests at University

 The use of multiple-choice tests in organic chemistry for first and second year university students.

 Gunstone, F.D. and Mackie, R.K.

 Educ. Chem., 4 (6) 272-276 (1967)
- The Origin of 'Normality'

 The concept of normal solutions was invented by the Scottish chemist Andrew Ure and developed by J.J. Griffin and K.F. Mohr. (14 references)

 Farrar, W.V.

 Educ. Chem., 4 (6) 277-279 (1967)
- Clos Activation of Cheap Organic Molecules

 The economics of the heavy organic chemicals industry and methods of activation.

 Davies, D.S. and Taylor, K.A.

 Educ. Chem., 4 (6) 289-292 (1967)
- Clo6 X-Ray Fluorescent Spectrography

 The theory and applications of X-ray fluorescent spectrography.

 Oliver, W.R.

 Educ. Chem., 4 (6) 295-298 (1967)
- Clo7 Organic Electrochemistry Part 1: Anodic Reactions of Carboxylic Acids

 The Kolbe electrosynthesis, the mechanism of the reaction and its synthetic applications. (15 references)

 Johnston, K.M.

 Educ. Chem., 4 (6) 299-303 (1967)
- The Recovery of Trace Elements after the Ozidation of
 Organic Material with 50 per cent Hydrogen Peroxide
 A quantitative investigation of the recovery of some 20 elements at the p.p.m.
 evaluation.

 Down, J.L. and Gorsuch, T.T.

 Analyst, 92 398-402 (1967)
- Clo9 The Use of 50 Per Cent Hydrogen Peroxide for the Destruction of Organic Matter for the oxidation of organic materials by the title reagent.

 Analyst, 92 403-407 (1967)

- C110 Explosion Hazards with Xenon Trioxide Solutions (Xenic Acid)

 Xenon trioxide has an explosive force comparable to that of TNT. Detailed safety precautions are given. These should be observed when using other xenon compounds since many of them hydrolyse to XeO3. (22 references)

 Holloway, J.H.

 Talanta, 14 871-873 (1967)
- Clll Precipitation of Nickel Dimethylglyoximate

 A study of the relative merits of homogeneous precipitation, the aqueous acetone precipitation and the conventional direct precipitation.

 Lyle, S.J. and Maghzian, R.

 Talanta, 14 1021-1028 (1967)
- Interference of the Ammonium Ion in Mohr's Method

 for the Determination of Chloride

 High results are obtained in the presence of ammonium ions. These were previously considered not to interfere if the pH was kept below 7.2. Ammonium ions should be removed by boiling with sodium hydroxide and then adjusting the pH.

 Block, J. and Water, O.B.

 Talanta, 14 1130-1131 (1967)
- The IR Spectrum of Sodium Hyponitrite

 The far infrared spectrum supports the trans-configuration for the N₂O₂²⁻ ion.

 Hughes, M.N.

 J. Inorg. Nuclear Chem., 29 1376-1377 (1967)
- Conversion of Fluorides into Chlorides, Bromides or Iodides

 Silicon tetrahalides are better than previously used reagents because of the greater differences in free energies of formation between SiF₄ and SiCl₄, SiBr₄ and SiI₄.

 Speeckaert, P.L.

 J. Inorg. Nuclear Chem., 29 1542-1544 (1967)
- The Thermal Decomposition of Ferrous Oxalate Dihydrate

 Thermogravimetric analysis and differential thermal analysis studies have shown that in vacuum or under nitrogen the decomposition produces anhydrous ferrous oxalate, stable up to 300°, followed by further decomposition to Fe₂O₃ and Fe₃O₄. The decomposition is very oxygen sensitive.

 J. Inorg. Nuclear Chem., 29 1599-1604 (1967) Nicholson. G.C.
- Recent developments in Calorimetry. Part 3
 Some Specific Types of Calorimeters

 Details of construction and some commercial instruments. (12 references)

 J. Chem. Educ., 44 (9) A688-A714 (1967)

 Wilhoit, R.C.

 ibid., 44 (10) A853-A882 (1967)
- Safety in the Chemical Laboratory
 Means of Contact and Entry of Toxic Agents

 Skin contact, inhalation and ingestion as means of body exposure to toxic

 agents.

 Stokinger, H.E.

 J. Chem. Educ., 44 (9) A721-A725 (1967)
- Instantaneous Precipitation from Homogeneous Solution

 A type of clock reaction which claims to show, for a brief time, the presence of type of clock reaction which claims to show, for a brief time, the presence of the yellowish-red triiodide ion before it forms a complex with polyethylene glycol.

 J. Chem. Educ., 44 (9) A727 (1967)

 Hiskey, C.F. and Cantwell, F.F.

JOURNALS AND PERIODICALS OF RELEVANCE TO CHEMISTRY TEACHING

REVUES ET PÉRIODIQUES INTÉRESSANT L'ENSEIGNEMENT DE LA CHIMIE

The following list of journals and periodicals includes both chemistry journals and publications of a more general educational and scientific nature which contain articles relevant to chemistry teaching. The editor would welcome information concerning titles and publishers inadvertently omitted from this compilation.

ARGENTINA/ARGENTINE

Anales de la Asociación Química Argentina. Asociación Química Argentina, Hipólito Yrigoyen 679, Buenos Aires.

AUSTRALIA/AUSTRALIE

Australian journal of chemistry. Commonwealth Scientific and Industrial Research Organization, 314 Albert Street, East Melbourne C. 2.

The Australian science teachers' journal. The Australian Science Teachers' Association, Sydney Teachers' College, Newtown, New South Wales.

AUSTRIA/AUTRICHE

Mitteilungen des Vereins zur Förderung des physikalischen und chemischen Unterrichts. Schelleingasse 39/10, Wien IV.

BELGIUM/BELGIQUE

Bulletin. Sociétés chimiques belges. 39, rue des Moutons, Louvain.

La liste de revues et périodiques ci-après comprend à la fois des revues de chimie proprement dites et des publications à caractère pédagogique et scientifique plus général contenant des articles qui se rapportent à l'enseignement de la chimie. La rédaction serait heureuse qu'on lui signale les omissions involontaires (titres et éditeurs) qu'elle pourrait avoir faites dans cette liste.

BRAZIL/BRÉSIL

Anais da Associação Brasileira de Química. Associação Brasileira de Química, Caixa Postal 550, Rio de Janeiro.

BULGARIA/BULGARIE

Biologiju i himija. Ministerstvo na prosvetata i Kulturata, Ul. W. Drumev 37, Sofia.

CANADA

Canadian chemical education. 151 Slater Street, Ottawa 4, Ontario.

Canadian journal of chemistry. National Research Council, Ottawa 2.

CHILE/CHILI

Boletín de la Sociedad Chilena de Química. Casilla 169, Concepción.

FINLAND/FINLANDE

Finska Kemistsamfundets Meddelanden-Suomen Kemistiseuran Tiedonantoja, Helsinki.

Suomen Kemistilehti. Finnish Chemical Society, Erottajankatu 1-3 A 11, Helsinki 13. FRANCE

Bulletin de l'Union des physiciens. 44, bd Saint-Michel, 75 Paris-6^e.

FEDERAL REPUBLIC OF GERMANY/RÉPUBLIQUE FÉDÉRALE D'ALLEMAGNE

Der mathematische und naturwissenschaftliche Unterricht (MNU). Deutscher Verein zur Förderung des mathematischen und naturwissenschaftlichen Unterrichts, 7500 Karlsruhe, Damaschkestr. 46.

GERMAN DEMOCRATIC REPUBLIC/RÉPUBLIQUE DÉMOCRATIQUE D'ALLEMAGNE

Chemie in der Schule. Verlag Volk und Wissen, 108 Berlin, Lindenstr. 54a.

Das Hochschulwesen, Verlag der Wissenschaften, Berlin.

GHANA

Ghana Association of Science Teachers bulletin. University College of Science Education, Cape Coast.

 ${\rm HUNGARY/HONGRIE}$

A kémia tanitása. Müvelödésügyi Minisztérium, Szalay utca 10-14, Budapest V. Journal of education, Szabadsag- ter 17, Budapest V.

 $_{\rm INDIA/INDE}$

Vigyan shikshak. All-India Science Teachers' Association, H.2/3, Model Town, Delhi 9.

ISRAEL

Israel journal of chemistry. Weizmann Science Press of Israel, P.O. Box 801, Jerusalem.

 ${\rm ^{ITALY}/ITALIE}$

Chimica. Istituto Italiano di Storia della Chimica, Via Quintino Sella 2, Milano.

 J_{APAN}/J_{APON}

Nippon kagaku zasshi. No. 5, 1-chome, Surugadai-kanda. Chiyoda-ku, Tokyo. Rika no kyôiku. Tôyôkan Shuppan-sha, 2-13 Kanda Awajichô, Chiyoda-ku, Tokyo.

MEXICO/MEXIQUE

Boletín del Instituto de Química. Universidad Autónoma de México, México D. F.

Revista iberoamericana de educación química. Sociedad Química de México, Ciprés 176, México 4, D.F.

NIGERIA

Journal of the Science Teachers' Association of Nigeria. Government College, Ibadan.

NETHERLANDS/PAYS-BAS

Chemisch Weekblad. Royal Netherlands Chemical Society, Burnierstraat 1, The Hague.

NEW ZEALAND/NOUVELLE-ZÉLANDE

Chemistry in action. New Zealand Institute of Chemistry.
P.O. Box 250, Wellington.

New Zealand school science. Westlake High School, Aukland, N. 2.

NORWAY/NORVÈGE

Norwegian journal of chemistry, mining and metallurgy. Kronprinsengatan 17, Oslo 1.

PERU/PÉROU

Boletín de la Sociedad Química del Perú. Casilla 891, Lima.

PHILIPPINES

Science bulletin. Science Foundation of the Philippines, 1580 Taft Avenue, Corner Herran, Manila.

POLAND/POLOGNE

Przemysł chemiczny. Zuravia 6/12, Warszawa. Chemia w szkole. Plac Dabrowskiego 8, Warszawa.

PORTUGAL

Revista Portuguesa de química. Sociedade Portuguesa de Ouímica e Física, Centro de Estudo de Química Nuclear, Instituto Superior Têcnico, Lisboa 1.

ROMANIA/ROUMANIE

Revue roumaine de chimie. Academiei R.P.R., Str. Gutenburg 3 bis, Bucuresti.

Stiința si tehnica. Comitetul Central al Uniunii Teneretubui Muncitor și Societatia pentru Raspindirea Stiinței si Culturii, Piața Scinteii 1, București.

SPAIN/ESPAGNE

Real Sociedad Española de Física y Química. Anales serie B: Quimica. Facultad de Ciencias, Ciudad Universitaria, Madrid 3.

SWEDEN/SUÈDE

Elementa. Stiftelsen Elementa, Mat. nat. sällskapet, Malma Ringy, 62B, Uppsala.

Svensk kemisk tidskrift. Farlag Svenska Kemist samfundet, Stockholm.

SWITZERLAND/SUISSE

Chimia. H. R. Sauerlander & Co. Lauwenzenvorstadt 89,

Mitteilungen der Vereinigung Schweitzerischer Naturwissenschaftslehrer. Verlag Sauerlander, 5000 Aarau.

TANZANIA/TANZANIE

START journal. Science Teachers' Association of Tanzania. St. Andrew's College, Minakai, Tanzania.

UGANDA/OUGANDA

Science teachers' journal. The Uganda Science Teachers' Association, P.O. Box 262, Kampala.

UNION OF SOVIET SOCIALIST REPUBLICS/UNION DES RÉPU-BLIQUES SOCIALISTES SOVIÉTIQUES

Himija v škole. Metodičeskij žurnal. Ministerstvo prosveščenija RSFSR, 3 proczd Marinoj Rości, 41 Moskva.

UNITED ARAB REPUBLIC/RÉPUBLIQUE ARABE UNIE

Majallat al-'Ulūm al-Hadīthah. Mabna al-Mujamma. Maydān al-Tahrīr, Cairo.

UNITED KINGDOM/ROYAUME-UNI

The school science review. Association for Science Education, 52, Bateman Street, Cambridge.

Education in chemistry. Royal Institute of Chemistry, 30 Russell Square, London, W.C.1.

The science teacher. Junior Club Publications Ltd., 60 Paddington Street, London, W.1.

UNITED STATES OF AMERICA/ÉTATS-UNIS D'AMÉRIQUE

Chemical and engineering news. American Chemical Society. 1155 Sixteenth Street NW, Washington D.C. 20936 Chemistry. Earlham College, Richmond, Ind.

Journal of chemical education. 20th and Northampton Streets,

Science teacher. National Science Teacher's Association, 1201 Sixteenth Street, N.W., Washington D.C.

VENEZUELA

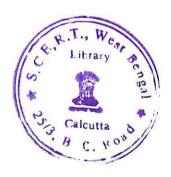
Revista de la Sociedad Venezolana de Química. Sociedad Venezolana de Química, Apartado 3895, Caracas.

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